MINING PHYSICS AND CHEMISTRY

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AND
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AUTHOR'S PREFACE

In the following pages there has been no attempt to deal with the more advanced portions of the subject matter, the book being of an introductory nature. For further information on Explosives the reader is referred to *Service Chemistry*, by Lewes and Brame, and for further information on the Chemistry of Coal to Professor Bone's book on *Coal and Its Scientific Uses*. The author's thanks are due to Mr. Bernard Whitaker, his brother, for the preparation of many of the diagrams, and to the following firms, who kindly supplied blocks for some of the figures: Messrs. Baird and Tatlock (London), Ltd.; Messrs. John Davis and Son, Ltd., All Saints Works, Derby; and the Cambridge and Paul Instrument Co., Ltd. In addition, the author has received invaluable assistance from Mr. Hunter, Head of the Mining Department of the Wigan Mining and Technical College, in the correcting of proofs and the suggesting of modifications, for which he wishes here to express his sincere gratitude.

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INTRODUCTION

By PROFESSOR W. H. McMILLAN

It is no exaggeration to state that the high position which we attained during the last century in the industrial world was built essentially on the foundation of an abundant supply of cheap coal; and to-day coal still remains by far the most important raw material of industry. To quote the eloquent words of one of our leading statesmen: "Coal is the most important element in our industrial life; the blood which flows through the veins of industry is made of distilled coal. King Coal is the paramount Lord of Industry. It enters into every article of consumption and utility. It is our real international coinage. We buy goods, food, and raw material abroad. We pay not in gold, but in coal. It not merely fetches and carries for us, but it makes the machinery and the material it transports."

The great strides made within recent years in the iron and steel industry, and the corresponding increase in the demand for fuel, compelled the mining engineer to effect many remarkable changes both on the surface and in the underground workings of his colliery. The modifications, indeed, were so numerous and of such a scientific nature that mining must now be reckoned among the foremost of the practical sciences. The future, moreover, will call for still greater developments. In the past there has been a tendency to work first that coal which is most easily and cheaply obtained, with the result that it is principally the deeper and thinner seams that have to be attacked in the future. Under these circumstances the cost of production will tend to rise unless all our skill and knowledge be brought to bear on the problems which confront us. This is absolutely essential; for any marked rise in price here will produce a serious setback to British industries in competition with those of other countries, especially where the latter are favoured with easily workable and therefore cheap coal.

To retain our industrial position, therefore, we must direct our attention to thorough investigation of the scientific aspects of the many difficult problems involved; and such attention must be given by *all* connected with the industry. The owner, manager, and underground worker must each take his proper share of the responsibility in the competitive fight. The mining industry is different from most other industries in that, no matter how much scientific skill be brought to its aid, there will always remain a considerable amount of danger. The attention which it has received from the Legislature has undoubtedly done much to reduce the number of accidents, but these are still frequent, and it is now recognised that greater immunity from danger can only be attained by raising the standard of education and training of the underground worker. Every individual descending a mine is responsible for the safety of all his co-workers, and it is therefore absolutely necessary that all should possess an intelligent knowledge of the physical and chemical conditions which prevail in the underground workings. No boy, for example, should be allowed to descend a safety-lamp mine without having previously been instructed in the principle of the lamp which he carries, and the great dangers which attend its ill-usage. Every underground worker should possess at least an elementary knowledge of the dangers which surround him—the occurrence and nature of the inflammable and noxious gases which may be present, the importance of efficient ventilation of the workings, the spontaneous ignition of coal, the explosibility of coal dust, and so forth. Rules and regulations may go some way to reduce the number of accidents, but the best results can only be obtained when the workers and minor officials understand the reasons for their introduction, and are able to utilise that knowledge efficiently in their daily duties.

The colliery manager has still greater responsibilities. While directing his attention to present conditions, he must at the same time give some thought to the future. Coal mining at greater depths, and the consequent increase in temperature of the workings, will call for more and more scientific knowledge. Methods of keeping the workings cool, of combating the greatly increased tendency to spontaneous ignition and explosions, and of dealing with the enormous pressures of the strata which may be experienced—all must sooner or later require his serious thought. Further, in order to enable him to control more efficiently the ventilation of the various districts underground and to obtain timely indication of any undue heating which may be taking place, periodic analyses of the mine air will become necessary.

Keen competition and economic pressure will also compel him to introduce methods of dealing efficiently and economically with the coal when raised to the surface. More attention must be devoted to the economical production of power. Water-softening and coal-washing plants, and methods of testing the coal for calorific value and other important qualites will become the rule rather than the exception.

Having read through the following pages in the light of many years' experience in the training of all types of mining students, I feel the book fills a great gap in modern coal-mining literature, and will be found invaluable to all engaged in the industry. It contains all the physical and chemical knowledge required of an efficient underground worker or official, and forms an excellent introduction to the many scientific problems which confront the colliery manager.

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UNITS OF LENGTH, AREA, VOLUME, AND MASS

Units of Length.

British Unit = 1 yard = 3 feet = 36 inches.

Metric Unit = 1 metre (m.) = 10 decimetres (dm.)
= 100 centimetres (cm.) = 1,000 millimetres (mm.).

Relation between British and Metric Units of Length:
1 metre = 39·37 inches. 1 inch = 2·54 centimetres.

Units of Area.

British Unit = 1 square foot = 144 square inches.

Metric Unit = 1 square centimetre = $\frac{1}{100}$ square decimetre.

Relation between British and Metric Units of Area:
1 square centimetre = 0·155 square inch.
1 square inch = $(2·54)^2$ square cm. = 6·45 square cm.

Units of Volume.

British Unit = 1 cubic foot = 1,728 cubic inches.

Metric Unit = 1 cubic decimetre (called *one litre*).
= 1,000 cubic centimetres (c.c.).

Relation between British and Metric Units of Volume:
1 litre = 61·02 cubic inches.
1 pint = 0·5682 litre. 1 gallon = 4·546 litres.
1 cubic inch = 16·387 cubic centimetres.

Units of Mass (see page 2 *et seq.*).

British Unit = 1 lb. avoirdupois = 16 ounces.

Metric Unit = 1 kilogram = 1,000 grams.
1 lb. = 453·6 grams. 1 oz. = 28·35 grams.
1 kilogram = 2·205 lbs.

Useful Data.

1 gallon of water weighs 10 lbs.
1 cubic foot of water weighs 62·4 lbs.

MINING PHYSICS AND CHEMISTRY

PART I.—PHYSICS

CHAPTER I

Forms of Matter.—Matter may be defined as that which our senses tell us exists. As we shall see later, all varieties of matter are supposed to consist of exceptionally small particles or **molecules.** To form an idea of the size of these molecules, we may consider Lord Kelvin's estimate—viz., that if a drop of rain were magnified to the size of the earth, the molecules would be of less size than cricket-balls!

There are three states of matter—**solid, liquid,** and **gaseous.** In a solid the molecules are practically at rest, and solid bodies retain their shape because of this. In a liquid the molecules are in a state of slow motion, the particles being able to tumble over one another. In a gas (such as air or firedamp) the molecules are in a state of rapid motion, moving about with enormous velocities; and by their bombardment of the walls of the containing vessel exert a pressure, so that a gas always tends to occupy a larger space.

Solids, then, have a definite size and shape. Liquids take the form of the containing vessel, and have a horizontal surface. Gases must be surrounded on all sides by the containing vessel. A gas introduced into any vacuous space will fill the space throughout, no matter how large it may be. Before proceeding to discuss some of the properties of matter it will be well to define "force."

Force.—If a body at rest is to be caused to move, some force must be employed. If a moving body is to be caused to come to rest or to change either its speed or the direction of its motion, some force must be employed. A weak force, however, may act on a stationary or on a moving body without either giving motion to the body at rest or affecting the motion of the moving body. Force is therefore defined as "that which *tends* to change the state of rest or of uniform motion of a body."

A force always acts in a straight line. This should be clear on a moment's thought. It is impossible to imagine a force acting in a curved path. If a body in its motion does not follow a straight line, the *total* force under which the body is moving is changing—possibly at every instant. When a stone is thrown *horizontally*, it is influenced by three forces:

1. The force used by the thrower, acting horizontally.
2. The force of gravity, acting vertically downwards.
3. The force of friction, or resistance to motion, offered by the air.

As a result of these forces the stone takes a gradually descending path to the earth, where the friction or resistance to motion offered by the ground soon brings the stone to rest.

The force of gravity has been mentioned above. This requires an explanation.

Gravitation.—Bodies fall to the earth because the earth attracts them. This is only a particular instance of the principle of gravitation, which states that "all bodies attract one another with a force which varies according to the 'masses' of the bodies, and also according to the distances the bodies are apart." The greater their "masses," the greater their attraction; but the greater their distance apart, the less their attraction.

Mass.—The mass of a body may be defined as the quantity of matter in the body, and is constant always. Now the earth, having so much a greater mass than the bodies or particles on its surface, attracts those bodies much more strongly than the bodies attract one another. The consequence is that all bodies tend to fall towards the earth, or, as we commonly say, bodies have weight.

Weight.—The weight of a body is, then, that force with which the earth attracts the body. Such force is not invariable, it is not constant, but depends on the mass of the body, and also upon the distance between the body and the earth's centre. But, more fully, the weight of a body varies inversely as the square of the distance between the body and the earth's centre.

An illustration may make this clear.

Imagine rays of light (which travel in straight lines) proceeding from the source *A* (Fig. 1) to the transparent plates *B* and *C*. *C* is twice as far from *A* as *B* is, and its area is four times the area of *B* in order that all the rays which fall on *B* may also just cover *C*. This can be verified either by experiment or by geometry; if by experiment, use a square wire figure for *B*, as the rays of light suffer some alterations in going through glass, etc. (If *C* had been three times as far from *A* as *B* was, the area of *C* would have had to be nine times the area of *B*, and so on, the area varying as the square of the distance.)

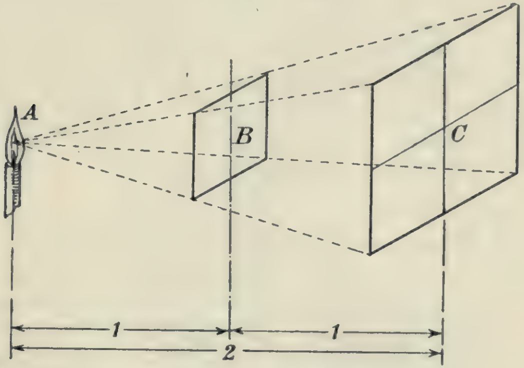


FIG. 1.—LAW OF INVERSE SQUARES.

Now, as all the light rays which fall on *C* also fall on *B*, and as the area of *C* is four times the area of *B*, it follows that the intensity of illumination—say, the amount of light or number of rays on one square inch—of *C* is only one-quarter of that of *B*. In other words, the intensity of illumination varies inversely as the square of the distance from the source of light. (In the case where *C* is three times as far from *A* as *B* is, the intensity of illumination on C is $\left[\left(\frac{1}{3}\right)^2=\frac{1}{9}\right]$ one-ninth of that on B.) Observe also that if this is true for any one direction, it is by similar argument true for all directions.

The force of gravity acts in a like manner. A body a certain distance from the earth's centre is attracted by the earth with a certain force. Double the above distance, and the body is then attracted only by one quarter of the above force. The differences in distance from the earth's centre met with even in moving from place to place on the earth's crust are sufficient to cause slight differences in the weights of an ordinary body. A body weighs less at the equator than at the poles—less at the top of high mountains than at sea level. There are also other conditions (such as the rotation of the earth) which cause differences in weight at different latitudes, but these may be neglected as their effects are likewise eliminated when an ordinary balance is used as a means for determining mass.

Units of Mass.—*The British Unit of Mass* is the pound. It is defined as the quantity of matter contained in a piece of platinum kept at the Standards Department, Board of Trade, Westminster. This mass is the one pound avoirdupois, or 1 lb.

The *French Unit* is similar to the British, but is about $2\frac{1}{5}$ times as large. It is the kilogram.

In scientific work the unit of mass is $\frac{1}{1000}$ of a kilogram—viz., 1 gram. (One cubic centimetre of water at 4° C. has a mass of 1 gram; and 1 lb. = 453·6 grams.)

How to Measure the Mass of a Body.—It has been stated that the pull of the earth on a body depends upon the mass or quantity of matter in the body, and also upon the distance of the body from the earth's centre.

I. Now, if two bodies at the same place are pulled by the earth with an equal force, it follows that, as the distance of each body from the earth's centre is the same, the bodies have equal masses. Also, if a body is counterpoised or balanced by certain "weights" (or, more correctly, "masses") in London, say, then the selfsame weights or masses will balance the body at any other place on the earth, above the earth, or in the earth as far as man is likely to penetrate. The weight or attractive force of the earth on the body may and does vary at different parts of the earth, but similarly the weight of the weights or masses varies and precisely to the same extent. The method employed for measuring the mass of a body is, then, by means of a balance. The pull of the earth on the body whose mass is required is balanced against the pull of the earth on the standard masses or weights.

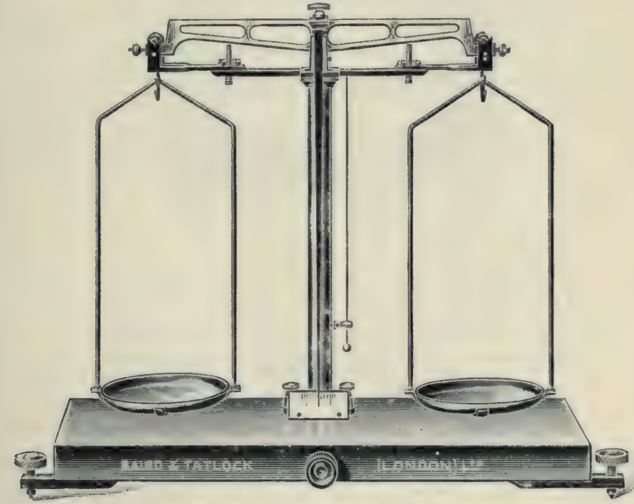


FIG. 2.—PHYSICAL BALANCE.

There are two types of scientific balances, the **Physical Balance** (Fig. 2) for fairly rough work, and the **Chemical Balance** (Fig. 3) for the more refined work. In either case, but especially when using a chemical balance, the pans should always be at rest and the beam supported off its pivot when weights or masses are being put on or taken off. *The balance is a most delicate and sensitive instrument and should be used* *with great care.* It is considerably more fragile and delicate than the sturdy material with which mining students are accustomed to deal, and this should always be borne in mind in working with it.

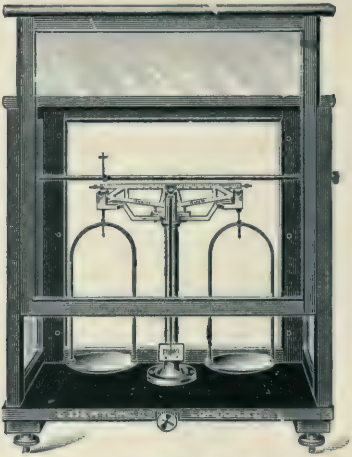


FIG. 3.—CHEMICAL BALANCE.

FIG. 4.—SPRING BALANCE.

II. **A Spring Balance** (Fig. 4) may also be employed for measuring—but only roughly—the mass of a body. The principle upon which balances of this type are constructed is that the extension of a spring is directly proportional to the force causing the extension. Now, this force is, in weighing a body, *not* the mass but the *weight* of the body, and this varies at different places on the earth. Accordingly, the spring balance registers accurately the weight but not the mass of a body, except at certain places. The error in the measurement of mass is small and, for most purposes, inappreciable, but nevertheless it exists.

The relation of "mass" to "weight" should now be clear. "Mass" is constant and "weight" is variable;

but, as we have seen above, the "weight" obtained by means of a true balance as in I. is an accurate measure of "mass" and not of "weight." In most everyday cases where we use the term "weight" we mean "mass." The latter word does not seem to be kindly taken to by the majority of us, and the distinction is not important except in scientific work and the like. The principle of gravitation was proved *experimentally* by Newton, who first stated it in his famous *Principia*.

Density.—"Lead is heavier than iron." But 2 lbs. of lead are not heavier than 2 lbs. of iron! What is meant is that, "bulk for bulk, lead is heavier than iron," or more exactly, "lead is *denser* than iron."

If a body weighs 10 lbs. and its volume is 2 cubic feet, the matter of which the body is composed is said to have a density of 5 lbs. per cubic foot. Density is defined as mass per unit volume, or—

$$\text{Density} = \frac{\text{mass}}{\text{volume}}.$$

Hence to find the density of a substance, it is necessary to obtain:

1. The mass of a piece of the substance.
2. The volume of this piece of the substance.

The mass is obtained by weighing on a balance.

The volume may be obtained by calculation if the solid is regular, or by other methods indicated below if the solid is irregular.

Volumes of Regular Solids.

Volume of a cube $= (\text{length of edge})^3$.
Volume of a rectangular block $= (\text{length} \times \text{breadth} \times \text{thickness})$.
Volume of a cylinder $= 3{\cdot}1416 \times (\text{radius})^2 \times \text{height}$.
Volume of a cone $= \frac{1}{3} \times 3{\cdot}1416 \times (\text{radius})^2 \times \text{height}$ (vertical).
Volume of a sphere $= \frac{4}{3} \times 3{\cdot}1416 \times (\text{radius})^3$.

Volumes of irregular solids may be found by:

1. Displacement of water in a graduated vessel.
2. Archimedes' Principle.

1. **Displacement Method.**—Introduce some water into a graduated glass vessel. Read the volume of the water (V_1). Completely immerse the solid whose volume is desired. The water will rise. Again read the volume (V_2). Then $V_2 - V_1$ is the volume of the solid; *e.g.*—

Initial reading $= 120$ c.c. $= V_1$.
Second reading $= 160$ c.c. $= V_2$.

Then the volume of the solid $= (160 - 120) = 40$ c.c. (1 c.c. = 1 cubic centimetre.)

2. **Archimedes' Principle.**—Fill a beaker with water and consider the forces acting on any cubic inch of the water (Fig. 5). This cube of water is supported by the rest of the water, otherwise it would sink and there would be currents in the liquid. There must therefore be a force acting upwards on the cube, and this force must be equal to the weight of the cube of water. Now if a cubic inch of copper, say, be put in the place of the cubic inch of water, and held there by a fine thread, there will be the same upward force acting on the copper. If the upper end of the thread be attached to a spring balance, the copper will weigh less in the water than in air, and the difference in weight will equal the weight of water displaced by the copper—in this instance, the weight of 1 cubic inch of water. To state the principle more generally: "A body weighs less in water than in air and the difference, due to the upthrust of the water, is equal to the weight of the water displaced by the body." The same is true for any other liquid, provided it has no chemical action on the body.

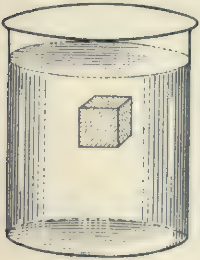


FIG. 5.

If, then, a body is weighed first in air and then in water and the loss in weight noted, this loss is equal to the weight of the water displaced; and, knowing the weight of this displaced water, its volume can easily be calculated, since 1 c.c. of water weighs 1 gram. This volume is, of course, the same as the volume of the solid causing the displacement. In carrying out determinations of the weight of a solid in water, a sensitive spring balance will be found convenient (Figs. 6 and 7). If it is preferred to use the ordinary balance, the solid is best suspended by the thread, as shown in Fig. 8, and a small bridge arranged to support the vessel containing the water in which the solid is immersed, *after first weighing the dry solid in air.*

FIG. 6.

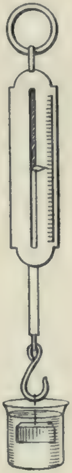


FIG. 7.

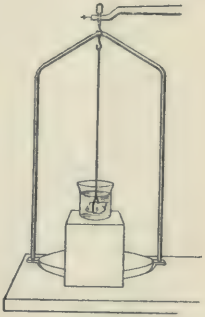


FIG. 8.

Example.—A piece of coal weighs 16 ounces in air and 4 ounces in water. What is the volume of the coal, being given that 1 cubic foot of water weighs 1,000 ounces ?

The loss in weight is $(16-4)=12$ ounces.

Now 1,000 ounces of water have a volume of 1 cubic foot or 1,728 cubic inches.

$\therefore$ 1 ounce of water has a volume of $\frac{1728}{1000}=1{\cdot}728$ cubic inches.

$\therefore$ 12 ounces of water have a volume of $1{\cdot}728 \times 12 = 20{\cdot}736$ cubic inches.

$\therefore$ The volume of the coal $= 20{\cdot}736$ cubic inches.

In this example the density of the coal is $\frac{16}{20 \cdot 736} = 0 \cdot 772$ ounces per cubic inch.

If a small piece of coal had been taken so that the above weights were in grams instead of ounces, the density of the coal could have been found as follows:

Weight in air = 16·00 grams.
Weight in water = 4·00 ,,

Loss in weight = 12·00 ,,

∴ Weight of water displaced = 12 grams.

But 1 gram of water has a volume of 1 c.c.

∴ 12 grams of water have a volume of 12 c.c.

∴ The volume of water displaced is 12 c.c., and this is also the volume of the coal causing the displacement.

The density of the coal is therefore $\frac{16}{12} = 1 \cdot 33$ grams per c.c.

In most of the laboratory determinations the weighings should be carried to the second or third decimal place of a gram—in other words, to the nearest centigram or milligram.

From the above, it is seen that Archimedes' Principle provides a very ready means of determining the density of a substance.

Specific Gravity.—The specific gravity of a substance is the number expressing how many times that substance is heavier than water, bulk for bulk. In other words, the specific gravity of a substance is a measure of how many times the substance is " denser " than water. The specific gravity of copper is 8·93, which means that copper is 8·93 times as heavy as water, bulk for bulk.

Now 1 cubic centimetre of water weighs 1 gram.

∴ 1 cubic centimetre of copper weighs 8·93 grams.

Or, the density of copper is 8·93 grams per c.c.

Similarly the density of iron is 7·8 grams per c.c., or its specific gravity is 7·8.

Clearly, the number which represents the specific gravity of a substance is also the number which represents the density of the substance in grams per c.c.; this is due to the fact that 1 c.c. of water weighs 1 gram.

Some important specific gravities are given below (temperature about 15° C. or 60° F.).

Liquids.		Solids.			
		Non-Metallic.		Metallic.	
Water ..	1·00	Cork ..	0·25	Aluminium	2·7
Petrol ..	0·70 (approx.)	Oak ..	0·84	Zinc ..	7·2
Alcohol ..	0·80	Coal ..	1·25–1·35	Tin ..	7·3
Benzene ..	0·88	Sand ..	2·6	Iron ..	7·8
Milk ..	1·03	Glass ..	2·6–3·1	Brass ..	8·4
Sea water ..	1·03	Felspar ..	2·6	Copper ..	8·9
Glycerine ..	1·26	Marble ..	2·7	Silver ..	10·5
Chloroform ..	1·47	Pyrites ..	4·5–5·0	Lead ..	11·4
Sulphuric acid	1·85				
Mercury ..	13·59				

In some cases the above figures are only approximate. Iron, for instance, has several forms, cast iron, wrought iron, etc., and each form has a particular specific gravity. Similarly with aluminium.

The Specific Gravity Bottle.—This is usually employed in determining the specific gravity of a liquid, though its use in finding the specific gravity of a solid is equally important.

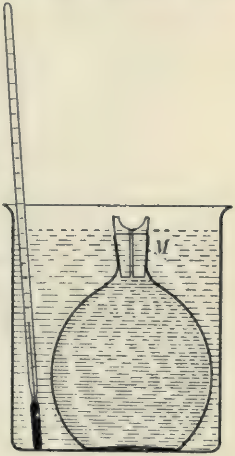


Fig. 9.—Specific Gravity Bottle.

The bottle (Fig. 9) has a pierced glass stopper, so that, if filled and the stopper inserted, the bottle will always contain the same amount of liquid, provided that the temperature is constant. The height of the liquid is adjusted to the mark *M* (in the pierced stopper) by absorbing any excess liquid with blotting-paper. It is desirable to have the stopper cup-shaped (as in diagram), so that when the liquid has been adjusted to *M* at the proper temperature in a bath, the bottle may be removed and wiped carefully (before weighing) without any fear of loss of liquid resulting from expansion due to the heat from the hand.

Specific Gravity of a Liquid.—The method will be clear from the following example;

Weight of stopper and dry empty bottle = 20·34 grams.

Weight of stopper and bottle full of water at 15° C. = 45·37 grams.

∴ Weight of water = 25·03 grams.

Weight of stopper and bottle full of liquid in question at 15° C. = 50·75 grams.

∴ Weight of liquid = 30·41 grams.

∴ Since the volumes of the liquid and water are the same, the specific gravity of the liquid $= \frac{30 \cdot 41}{25 \cdot 03} = 1 \cdot 21$.

(See 1 and 2 below for precautions in connection with change of temperature.)

Specific Gravity of a Solid by Means of the Specific Gravity Bottle.—In order to obtain accurate results care is necessary in the following particulars:

1. The volume of the liquid in the specific gravity bottle must be adjusted after the bottle has stood for some minutes in a water bath at the desired temperature before removing the bottle from the bath.

2. The bottle must be wiped quite dry before weighing.

3. In order to avoid air-bubbles the solid, while it must necessarily be in small pieces in order to be capable of being introduced into the bottle, should not be powdery, and the water should easily "wet" the surfaces of the solid.*

The method of procedure will be clear from the following example. Four weighings are necessary, and they are best done in the order given, provided the bottle is dry to start with:

---

* In certain cases it may be necessary to substitute another liquid (such as paraffin oil) for water, due allowance being made for the specific gravity of the liquid in the final calculation.

(*a*) Weight of stopper + dry empty bottle = 22·24 grams.
(*b*) Weight of stopper + dry empty bottle + solid = 32·44 ,,
(*c*) Weight of stopper + dry empty bottle + solid + water to fill at 15° C. = 54·75 ,,
(*d*) Weight of stopper + bottle full of water at 15° C. = 47·26 ,,

Weight of water to fill bottle $(d-a)$ = 25·02 ,,
Weight of solid $(b-a)$ = 10·20 ,,
Weight of water to fill bottle when solid is also in bottle $(c-b)$ = 22·31 ,,

∴ Weight of water displaced by the solid = 25·02 − 22·31 = 2·71 grams.

∴ Volume of water displaced by the solid = 2·71 c.c.

∴ Volume of solid = 2·71 c.c.

∴ Density of solid $= \frac{\text{mass}}{\text{volume}} = \frac{10{\cdot}20}{2{\cdot}71} = 3{\cdot}76$ grams per c.c.

In other words, the specific gravity of the solid is 3·76.

Flotation.—A body floats when the upthrust of the liquid on the body (see Archimedes' Principle) is equal to the weight of the body.

In the first case, suppose a body remains, of its own accord, just suspended at any position in the liquid in which it is completely immersed. Then from Archimedes' Principle the force of the upthrust is equal to the weight of liquid displaced. But this is clearly equal to the weight of the body. That is to say, equal volumes of the body and the liquid have the same weight. The solid and the liquid therefore have the same density. If the liquid were water, then the specific gravity of the solid would be unity.

In the second case, suppose the body, a piece of wood, say, floats with three-quarters of its volume under water, and one-quarter above. Now the whole weight of the wood is being borne by the upthrust of the water. This, we know, is equal to the weight of the water displaced, which is a quantity of water whose volume is three-quarters that of the wood. In other words, a certain volume of wood has a mass equal to the mass of three-quarters of that volume of water, or the specific gravity of the wood is $\frac{3}{4}$ or 0·75. Similarly, if an iceberg floats with $\frac{9}{10}$ of its volume below water, the specific gravity of iceberg ice is $\frac{9}{10}$ or 0·9 (neglecting the correction necessary on account of the specific gravity of sea water being slightly greater than unity).

Hydrometers. — Ordinary hydrometers are instruments for measuring the specific gravities of liquids directly by flotation.

An hydrometer consists of a small glass bulb (usually weighted with mercury or lead shot) communicating with a larger bulb above, to which is attached a long graduated stem closed at the top. The less "dense" the liquid, the farther will the stem be immersed.

The graduation on the stem which coincides with the level of the surface of the liquid is read.

In the **Universal** type (Fig. 10) this reading gives the specific gravity direct. In the **Twaddell** type (Fig. 11) it is necessary to multiply the reading by five, then add 1,000, and finally divide by 1,000. In symbols:

Specific gravity

$$= \frac{(\text{degs. Twaddell} \times 5) + 1000}{1000}.$$

FIG. 10.—UNIVERSAL HYDROMETER.

FIG. 11.—TWADDELL HYDROMETER.

E.g., in a strong sulphuric acid solution a Twaddell hydrometer gave a reading of 166. What is the specific gravity ?

$$166 \times 5 = 830.$$
$$830 + 1000 = 1830.$$
$$\frac{1830}{1000} = 1{\cdot}830 = \text{true specific gravity.}$$

Hydrometers are often supplied in sets in order to cover a wide range of specific gravities with accuracy.

Nicholson's Hydrometer (Fig. 12) may be employed for determining the specific gravity of solids. It may also be conveniently used for weighing light bodies. It consists of a top tray C supported on a stem, joined to a large hollow cylindrical body A, which supports at its base another small tray B. This tray is weighted so that the instrument will float in water with a small portion of the cylindrical body above the surface of the water. The whole instrument is made of metal. A mark, P, is scratched on the stem an inch or so below the top tray.

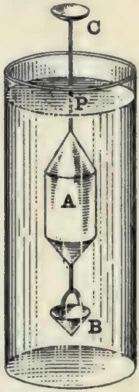


Fig. 12.—Nicholson's Hydrometer.

The simplest use of the hydrometer is to weigh a light body. Weights (w_1) are put on the top pan to sink the hydrometer till the mark P is level with the top of the liquid. The weights are then removed, and the body is placed on the top pan together with such weights (w_2) as are now necessary to sink to the mark. Then the weight of the body will be given by $(w_1 - w_2)$.

The common use of the hydrometer is to find the specific gravity of a solid. The above weights (w_1 and w_2) having been noted, transfer the solid to the lower pan, and add weights (w_3) on the top pan to sink to the mark. On account of the upthrust of the water, the weights necessary to sink to the mark when the solid is immersed (*i.e.*, on the lower pan) will clearly be greater than when the solid was on the upper pan. That is, w_3 is greater than w_2.

Also $(w_3 - w_2)$ is the amount of the upthrust.

$\therefore$ $(w_3 - w_2)$ is the weight of liquid displaced.

If the liquid is water and the weights are in grams, then, since 1 gram of water has a volume of 1 c.c., the volume of $(w_3 - w_2)$ grams is $(w_3 - w_2)$ c.c. And this must be the volume of the solid which displaced the water.

The density of the solid is, then, $\frac{w_1 - w_2}{w_3 - w_2}$ grams per c.c., or its specific gravity is $\frac{w_1 - w_2}{w_3 - w_2}$. *E.g.*—

$$\begin{aligned} w_1 &= 30{\cdot}5 \text{ grams.} \\ w_2 &= 15{\cdot}5 \quad ,, \\ w_3 &= 23{\cdot}5 \quad ,, \end{aligned}$$

Weight of solid $= w_1 - w_2 = 30{\cdot}5 - 15{\cdot}5 = 15$ grams.

Weight of water displaced $= w_3 - w_2 = 23{\cdot}5 - 15{\cdot}5 = 8{\cdot}0$ grams.

∴ Volume of water displaced = 8 c.c. (1 c.c. of water weighs 1 gram).

∴ Volume of solid = 8 c.c., and specific gravity of solid $= \frac{15}{8} = 1{\cdot}875$.

If the solid is lighter than water—*i.e.*, its specific gravity is less than unity—it will be necessary to fix it to the lower pan. This may be done by means of a rubber band, which, however, must be fastened to the lower pan during the whole experiment. In such a case w_3 will clearly be greater than w_1. *E.g.*—

$$\begin{aligned} w_1 &= 30{\cdot}2 \text{ grams.} \\ w_2 &= 25{\cdot}4 \quad ,, \\ w_3 &= 35{\cdot}4 \quad ,, \end{aligned}$$

$$\text{Specific gravity: } \frac{w_1 - w_2}{w_3 - w_2} = \frac{30{\cdot}2 - 25{\cdot}4}{35{\cdot}4 - 25{\cdot}4} = \frac{4{\cdot}8}{10{\cdot}0} = 0{\cdot}48.$$

Specific Gravity and Density Applications.—Coals may be roughly classified according to their specific gravities.

Lignites have a specific gravity usually about 1·1–1·2; ordinary British (bituminous) Coals of 1·25–1·35. The specific gravity of Anthracites, however, may rise to 1·5 or

1·6. Oil Shales have a specific gravity usually lying between 1·3 and 2·2, whereas ordinary shales average from 2·5 to 2·8.

The specific gravity of mineral oil varies, but is always less than 1·0. The specific gravity of minerals often serves as a useful property for distinguishing them.

Most valuable ores have a specific gravity considerably greater than 2·6, which is the average specific gravity of the rocks forming the earth's crust. *E.g.*—

	Sp. Gr.
Galena	=7·6
Copper pyrites	=4·0
Iron Ores:	
Iron glance	=5
Magnetite	=5
Limonite	=3·6–4
Siderite	=3·8

	Sp. Gr.
Stibnite (antimony sulphide)	=4·6
Zinc blende	=4
Tinstone	=7
Wolfram (ore of tungsten)	=7–7·5

In separating an ore from its impurities, washing is often resorted to, advantage being taken of the *higher* specific gravity of the ore. In coal-washing, the separation of coal from its associated impurities depends in the first place upon the *lower* specific gravity of coal, and secondly upon the fact that when a body is allowed to fall freely in water it reaches, in the first second of its fall, a maximum velocity governed by (1) the specific gravity of the body, and (2) its size and shape.

In symbols— $V = k\sqrt{l(s-1)}$

where V = velocity (maximum); k = a constant; l = diameter of the body (the spherical being the ideal shape); s = specific gravity of the body.

By screening the material before washing the particles are reduced to similar size and shape. Such particles, when allowed to fall in water, will have various maximum velocities dependent upon the specific gravities of the different substances, the coal being the slowest in descent. Further, since it is during the first second of fall that the various maximum velocities are reached, and also because of the impeding effects due to congestion of particles in the washer, the water is commonly given a pulsatory movement, and better separation is thus obtained.

CHAPTER II

Pressure of Fluids.

Pressure of Liquids.—A liquid in a vessel exerts a pressure in all directions.

If a hole be bored in the bottom of the vessel, the liquid will flow out, proving there is a downward pressure.

The same occurs if a hole be bored in the side of the vessel, which proves there is a pressure sideways. The following experiment is instructive.

Take a cylindrical lamp globe (Fig. 13) and close the bottom by a light metal plate held in position by a thread as shown. Take a large glass vessel and fill three quarters of it with water and introduce the lamp globe. As soon as the cylinder is depressed into the water the thread may be released, and the metal plate will adhere to the lamp globe. This shows that the liquid exerts a pressure upwards. Now it will be found that water may be poured into the cylinder without displacing the metal plate, until the column of water in the lamp globe reaches the level of the water outside.

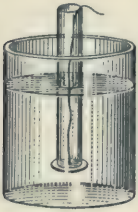


Fig. 13.

This proves that at any particular depth the pressure upwards of a liquid is equal to the pressure downwards.

The pressure at any point in a liquid depends upon the vertical depth of the point below the free surface (*i.e.*, the surface exposed to the air). The pressure acts in every direction around the point, and its value may be found as follows:

To find the pressure at P in Fig. 14, imagine a column of liquid which stands on unit surface (say 1 square cm.). This column is built up of a number of cubes, each cube having

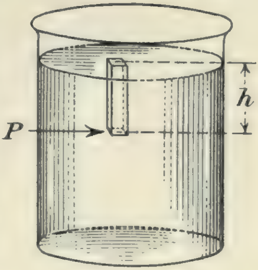


FIG. 14.

unit volume (in this case 1 c.c.). Let the number in the column be *h*—*i.e.*, the length of the column is *h* cm. Now the weight supported at *P* is the sum of the weights of each cube of the liquid, and this weight is the cause of the pressure on the area at the base of the column. But the mass of each unit cube of the liquid is the density of the liquid; density being the mass of unit volume. Therefore the mass of the whole column in grams is $h \times d$ (where *d* is the density in grams per c.c.); or the pressure on the unit area at depth *h* is $h \times d$. To obtain the total pressure on a surface of area *A* square units, we must multiply the pressure at the given depth by the number of units of area in the surface —*i.e.*, pressure at a depth $h = h \times d \times A$. *E.g.*, find the pressure on an area of 5 square feet, at a depth of 9 feet 6 inches, the density of water being 62·4 lbs. per cubic foot. Pressure = $9{\cdot}5 \times 62{\cdot}4 \times 5$ lbs. = 2964 lbs.

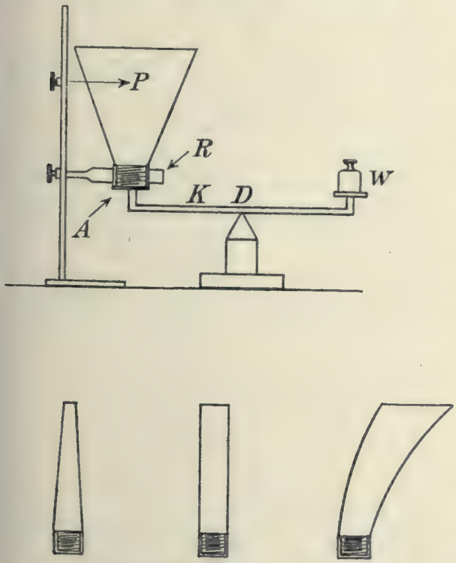


FIG. 15.—PASCAL'S VASES.

The pressure on a certain area at any depth of a liquid can be shown to be independent of the volume or shape of the containing vessel by means of **Pascal's Vases** (Fig. 15).

These are vessels whose base areas are equal but whose volume and shape are entirely different. The bottom of each vessel is fitted with a metal collar, which can be screwed into a metal ring *R* on the stand. A rubber pad *A*, attached to the arm *K*, forms one pan of the balance (whose fulcrum is at *D*). A convenient weight *W* on the other pan keeps the pad in position, and water poured into the vase until the pressure of the water is sufficient to overbalance weight *W*, water then escaping round the pad. The height of the water is noted and the pointer, *P*, adjusted to it. One of the other vases is then screwed into position and water introduced as before. In each case the height indicated by *P* is found to be the same.

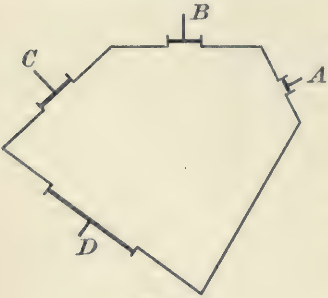


FIG. 16.

It is clearly **the "head" of the water which is responsible for the pressure, and not the volume of the water or its weight.**

Liquids also transmit Pressures in all Directions.—If the vessel *ABCD* (Fig. 16) be filled with water, and a pressure of 1 lb. be exerted on the piston *A*, whose area is 1 square inch, then the pressure on the pistons at *B*, *C* and *D* will be proportional to their areas.

If the area at *B* is 4 square inches, the pressure at *B* will be 4 lbs.

If the area at *C* is 10 square inches, the pressure at *C* will be 10 lbs.

If the area at *D* is 16 square inches, the pressure at *D* will be 16 lbs.

FIG. 17.—HYDRAULIC PRESS.

The above fact is made use of in the **hydraulic press** (Fig. 17), where, by exerting a comparatively small pressure on a small area of water (*A*), a very large pressure is developed on the large area (*B*). The pressure per unit area is, of course, the same at either end, but the area of one end being much greater than that of the other, the total pressure in the former case is much greater than the total pressure in the latter.

It may be seen from above that if a bottle is filled completely with liquid and the stopper then inserted, even with ordinary pressure an enormous total pressure is developed on the glass of the bottle—sometimes sufficient to break it. For this reason it is advisable always to leave a small air space above the liquid in a bottle before inserting the stopper.

Level Surfaces of Liquids.—It is well known that a liquid enclosed in a pipe "finds its own level" (Fig. 18).

On this principle water is supplied to houses, etc., the reservoir from which it flows being at a higher level than the houses.

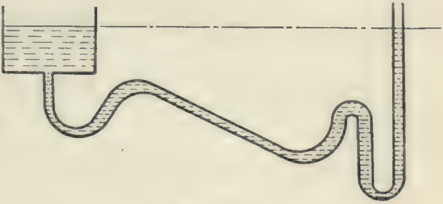


Fig. 18.

U-Tube Experiments.—Take a U-tube and pour some water down one limb. Observe that the height of the water in each limb is always such that the surface of the liquid is horizontal whether the U-tube be inclined or not (Fig. 19).

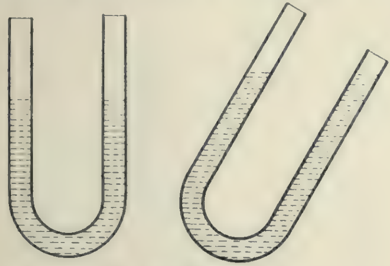


Fig. 19.

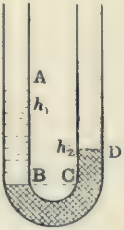


Fig. 20.

If, however, a denser liquid such as mercury be poured down one limb, then the free surfaces are no longer horizontal when the liquids come to rest. Considering, however, the pressures at B (Fig. 20), the downward pressure of the water must equal the upward pressure of the mercury. Now the water pressure is due to the head of water, h_1; and the mercury pressure is due to the head of mercury, h_2.

If, therefore, d_m be the density of mercury and d_w that of water, then

$$d_m \times h_2 = D_w \times h_1;$$

or

$$d_m = \frac{h_1}{h_2 \times 1}$$

(the density of water being 1 gram per c.c.) or the density of mercury

$$= \frac{\text{(height) of water column}}{\text{(height) of mercury column}}.$$

The mercury at the bottom of the tube may be regarded as a balance, supporting equal forces on each arm—on the one side a certain pressure of mercury, on the other a certain pressure of water.

Water Gauge or Manometer.—A U-tube may be used as a water gauge, sometimes termed, more correctly, a pressure gauge or manometer.

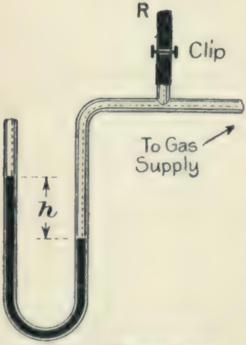


Fig. 21.—Manometer.

If one limb of the U-tube (Fig. 21) be connected to the gas supply, the clip at *R* being open, the water will be at the same height in both limbs. If, now, the gas be turned on and the clip closed, the water will be depressed in one limb and raised in the other. The difference in height is a measure of the difference of pressure on the surfaces of two columns of water. Let the difference be 3 inches.

Now 1 cubic foot of water weighs 62·4 lbs.

$\therefore$ 1 ,, inch ,, ,, $\frac{62{\cdot}4}{1728}$ lbs.

$\therefore$ 1 inch column of water exerts a pressure of $\frac{62{\cdot}4}{1728}$ lbs. per square inch.

∴ The pressure from a column of water 3 inches high is $\frac{3 \times 62{\cdot}4}{1728}$ lbs. per square inch;

or $$\frac{3 \times 62{\cdot}4 \times 144}{1728} \text{ lbs. per square foot.}$$

Note.—This, it must be clearly understood, is the difference of pressure in the two limbs and not the absolute pressure acting on one limb.

One inch of water column corresponds to a pressure of $\frac{62{\cdot}4}{1728}$ lbs. per square inch

$$= \frac{62{\cdot}4 \times 144}{1728} \text{ lbs. per square foot}$$

$$= \frac{62{\cdot}4}{12} = 5{\cdot}2 \text{ lbs. per square foot.}$$

It is convenient to remember this figure in calculations of ventilating pressure and the like where the water gauge is given. In mining practice the ventilation is commonly produced by means of a fan, either a force fan or a draught fan. The fan in either case is merely a mechanical contrivance for producing difference in pressure and consequently causing air currents. This difference of pressure is commonly expressed as so many inches of water gauge. To convert inches of water gauge to pressure in pounds per square foot it is only necessary, as stated above, to multiply by 5·2. An ordinary water gauge is shown in Fig. 22.

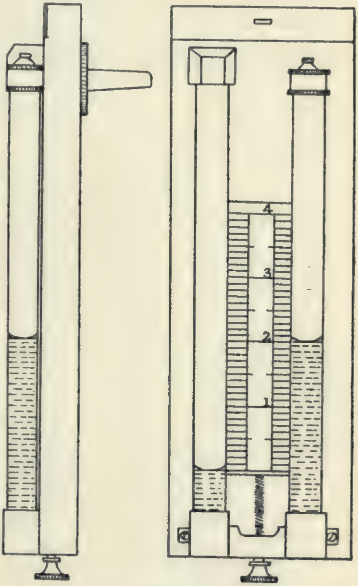


Fig. 22.—Water Gauge.

A Recording Water Gauge on the principle of the Aneroid Barometer and Barograph (see pp. 27 and 28) is shown in Fig. 23.

The corrugated metal box which is partly evacuated expands and contracts with fluctuations of the pressure in the fan drift, and these fluctuations are transferred by the mechanism to the pen and registered on the chart, which is revolved by clockwork at the proper rate.

Pressure of the Atmosphere.—The gases of the atmosphere are fluids, and like any other fluids (*e.g.*, water) they exert a pressure on any surface immersed in them. This pressure is due to the weight of a column of gas (air) standing on that surface. That the air has weight can easily be shown by weighing a globe (of volume about ½ cubic foot) and then evacuating it (that is, extracting all the air) by an air pump and weighing again. One cubic foot of air under ordinary conditions weighs about 1¼ ounces.

The earth is spherical in shape, and on its surface is an envelope of air, which gradually thins out the farther it lies from the earth. This envelope, however, may roughly be taken as fifty miles in height. On unit area of the earth's surface—say 1 square foot—there is therefore supported the weight of a column of air of about fifty miles in height, and it is this weight which is known as the pressure of the atmosphere.

Since the column of air to be supported at the top of a mountain is not so high as at the bottom, we should expect the pressure of the atmosphere at the top to be less than at the bottom. This is found to be the case.

By similar reasoning the atmospheric pressure at the bottom of a pit shaft is greater than at the surface. That the atmosphere does exert a pressure can be shown in a number of ways.

If a box made of very thin metal be evacuated (by means of an air pump) the sides of the box will collapse. Before evacuation the pressure of the air inside the box was balancing the pressure of the air outside. After evacuation there is no such inside pressure to withstand the pressure of the air outside and, the metal not being strong, the sides of the box are pressed together and the box is contorted.

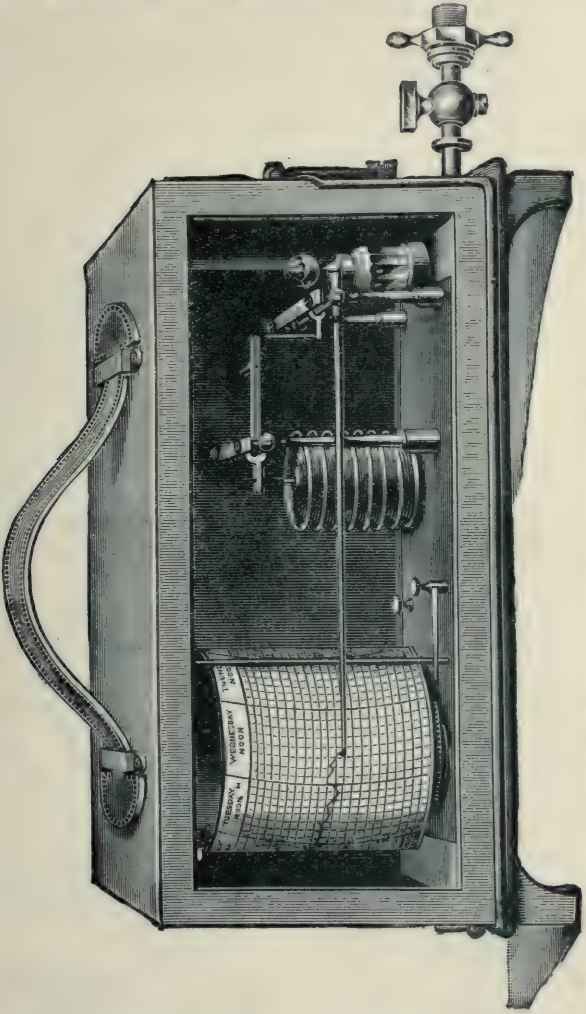
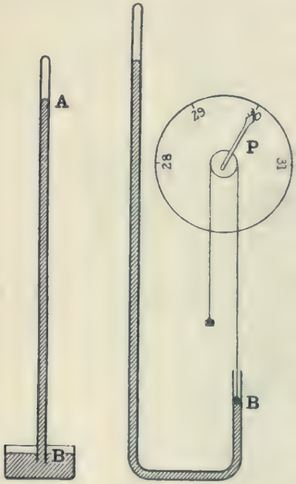


FIG. 23.—EDNEY'S SELF-RECORDING MINE VENTILATION GAUGE.

The Barometer.—In order to measure the pressure of the atmosphere an instrument called a " barometer " is employed.

To make a simple barometer take a stout glass tube about a yard long, closed at one end, and fill it completely with mercury. Close the open end with the finger and take care that no air is enclosed between the finger and the surface of the mercury. Now invert the tube and place the open end beneath the surface of some mercury in a basin or trough (Fig. 24*a*). Remove the finger and support the tube by means of a retort stand.



(*a*) (*b*)

Fig. 24.—Barometer.

The mercury column falls until the vertical height (*AB*) of the mercury surface in the tube is about 30 inches above the surface of the mercury in the basin. Observe that even if the glass tube be inclined, the mercury will preserve the same vertical height (Fig. 25). The pressure of this column of mercury (of about 30 inches or 760 millimetres) balances the pressure of the atmosphere acting on the surface of the mercury in the basin. The method of recording the pressure by a pointer (*P*) on a dial, as usually carried out in ordinary barometers, is shown in Fig. 24*b*.

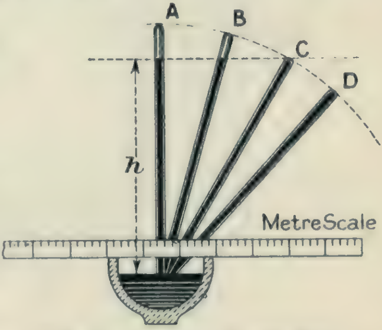


Fig. 25.—Aneroid Barometer.

The vacuum at the top of a barometer is called the Torricellian vacuum, and it contains only traces of mercury vapour. Torricelli, about the year A.D. 1643, made the first mercury barometer.

[*Note.*—If a little air or moisture is enclosed in the barometer tube, the pressure shown by the mercury column will be less than atmospheric.] Now the mercury in the basin is being pressed upon by the atmosphere on one side and by the mercury column on the other, and these two pressures balance each other. In the case of compression of a liquid, such as this, we have seen (p. 20) that the pressure on unit area (say the pressure in pounds on one square inch) is the same on all the surfaces of the liquid, and this pressure must be equal to that of the atmosphere in pounds per square inch.

Now, if the cross-sectional area of the tube had been 1 square inch, the mercury would have been at exactly the same height in the tube and the pressure of the column of mercury would have been $30 \times 0{\cdot}491$ lbs. (assuming the height to be 30 inches) $= 14{\cdot}73$ lbs. (0·491 lb. is the weight of 1 cubic inch of mercury). The pressure of this mercury column, we have seen, is balancing the pressure of the atmosphere. It follows then that the **atmospheric pressure in pounds per square inch =height in inches of " barometer " × 0·491.**

It is roughly **about 15 lbs. per square inch,** and it is subject to some variation due to changes in atmospheric conditions and in elevation.

A pressure of three atmospheres is then roughly $(3 \times 15) =$ 45 lbs. per square inch. (Corrections due to changes in temperature, which affect the density of the mercury, are necessary for very accurate work.)

The Aneroid Barometer and the Barograph.—The Aneroid Barometer (Fig. 26) is another instrument for measuring the pressure of the atmosphere, and its action is possibly more easily understood than is that of the mercury barometer. Moreover, it answers more readily to changes in pressure than does the mercury barometer, which, unfortunately, has some tendency to lag behind atmospheric changes. It consists of a corrugated metal box partly evacuated. Increases in atmospheric pressure cause the box to be compressed and decreases cause expansion. These fluctuations are registered by means of a finger which is attached to appropriate mechanism communicating with the evacuated box.

Aneroid barometers have the disadvantage that they require standardising periodically. Self-recording aneroid barometers or barographs (Fig. 27) are now coming very much into favour and should be particularly useful at collieries where daily readings of the barometer have to be recorded. The great advantage of this type of instrument, however, is that from the graph which it draws the tendency of the fluctuations can be seen and the changes anticipated. This is important, as when the pressure of the atmosphere is falling there is a tendency for the gases to escape from the waste and old workings into the open roadways of the mine, and special caution is at such times necessary.

Fig. 26.—Ordinary Aneroid Barometer.

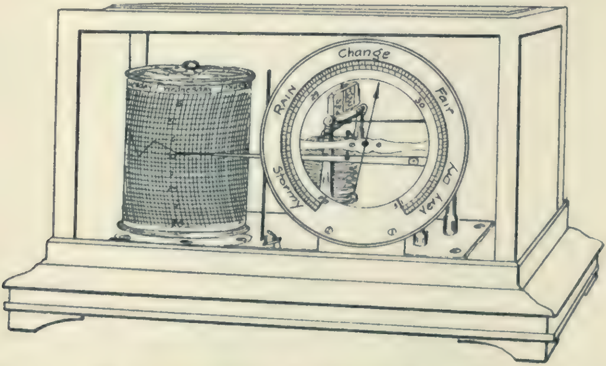


Fig. 27.—Aneroid Barometer Barograph.

Hare's Density Method.—Hare's apparatus for finding the specific gravities of liquids consists of an inverted U-tube to which there is attached about the middle of the bend a short tube with a clip (Fig. 28). A scale is affixed alongside. One limb passes into a beaker of water, the other into a beaker containing the liquid whose specific gravity it is desired to ascertain.

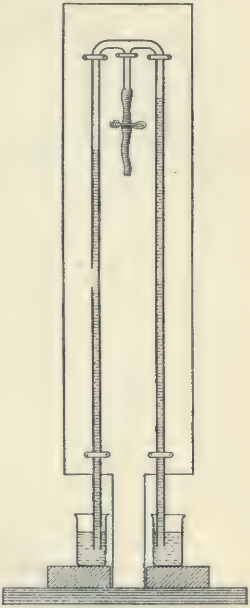


Fig. 28.—Hare's Apparatus.

The clip is opened and some of the air is withdrawn (by the mouth) from the apparatus and the clip then closed. The pressure of the air inside the apparatus is now less than the air pressure outside acting on the surfaces of the liquids in the beakers. The liquids are therefore forced up the limbs until a balance is obtained. The specific gravity of the liquid tested = $\frac{\text{height of water}}{\text{height of liquid}}$, the heights being measured from the free surfaces in each case—*i.e.*, from the surface of the liquid in the beaker.

E.g., to find the specific gravity of a solution of salt:

Height of Water.	*Height of Salt Solution.*	*Specific Gravity of Solution.*	
36·1 cm.	31·4	$\frac{36\cdot1}{31\cdot4}=1\cdot15$	Average value $=1\cdot15$
40·3 ,,	35·2	$\frac{40\cdot3}{35\cdot2}=1\cdot14$	
48·3 ,,	41·4	$\frac{48\cdot3}{41\cdot4}=1\cdot16$	

The Suction Pump or Bucket Pump (Fig. 29).—The principles on which these pumps work are as follows:

The valves at *A* and *B* open upwards only. When the bucket *CD* is forced downwards any water between *A* and *B* will pass through valve *A* on to the top side of *CD*, for it cannot pass through valve *B*. Now as *CD* is raised the water above it closes valve *A*, and this water is carried upwards and delivered into a tank. The space between *CD* and *B* would now be a vacuum were it not for the fact that the atmospheric pressure acting on the surface XY of the water in the sump forces the water up the pipe, past valve *B* into the space referred to. On the descent of *CD* the whole process is repeated. The supply of water from such a pump is clearly intermittent.

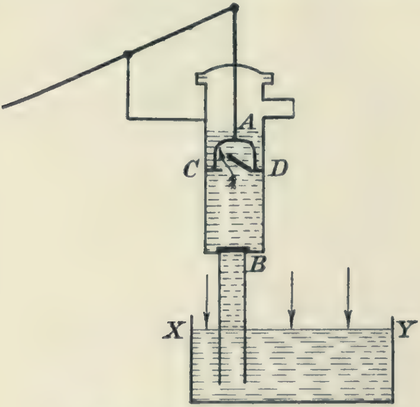
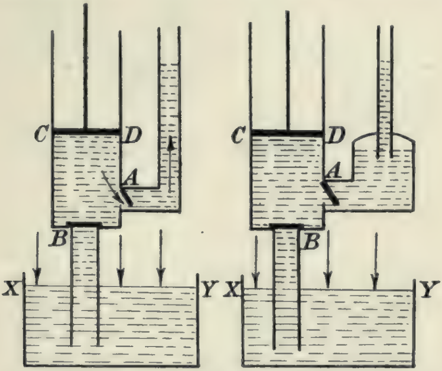


FIG. 29.—SUCTION PUMP.

The Force Pump, Plunger Pump, or Ram Pump (Figs. 30 and 31).—As before, there are two valves, *A* and *B*, both of which open upwards, but valve *A* is placed in a different position from that which it occupies in the suction or bucket pump. Also valve *A*, instead of being "lifted" upwards, is "forced" upwards.

On raising the plunger CD, valve A is closed by the atmospheric pressure if the pump is being started up; if the pump has been already working the water in the rising main closes valve A. Valve B opens and a vacuum tends to be formed in the space between CD and B, and also in the pipe below B. The atmospheric pressure, however, acting on the surface of the water in the sump, forces the water up the pipe and into the said spaces. On the downstroke of the plunger CD, valve B naturally closes, and water is forced through A, into the rising main, to be delivered at some convenient place.



Figs. 30 and 31.—Force Pumps.

Air vessels (Fig. 31) are often fitted to plunger pumps in order to provide a " cushion " and so avoid damaging the pump on the change of stroke. Water is practically incompressible, and some means must be adopted to absorb the shocks due to alternate stopping and starting in motion of the water. The maximum height at which valve B may be placed above surface XY of the water in the sump, either with suction or force pumps, is of interest and importance in practice.

It has been seen that the water is raised solely by the pressure of the atmosphere until it passes beyond valve B. Now the atmospheric pressure will, under normal conditions, support a column of mercury 30 inches high, and mercury is 13·6 times as dense (heavy) as water. The height of water column, therefore, that the pressure of the air will support is $30 \times 13{\cdot}6$ inches or $\frac{30 \times 13{\cdot}6}{12}$ feet—roughly 34 feet. Hence a water barometer would be about 34 feet long. On the top of a mountain, the water column would be, naturally, much less, and at the bottom of a deep shaft the column would be greater. In a theoretically perfect pump 34 feet is roughly the maximum height to which water may be raised (by means of the atmospheric pressure) from the sump to the first valve. Due to friction losses and imperfect vacuum arising from imperfect fitting of the bucket in the working barrel and also because of the " clearance volume " necessary in the pump, an average maximum height for practice is about 20 feet.

This height of 20 feet is liable to variation as the atmospheric pressure varies. In coal-mine workings in general, the mines being sometimes at considerable depths from the surface, the increase in atmospheric pressure is in favour of allowing a greater maximum height at which valve *B* may be situated above the surface of the sump water. On the other hand, metal-mines are often in mountainous districts where the atmospheric pressure is low, and this may necessitate the reduction of the said height. Temperature changes of the water being pumped also affect the question somewhat, as water is less dense at warm temperatures than at cold. Also solids (such as common salt) dissolved in the water increase its density, and if present in quantity may be of importance.

The above height must not be confused with the height to which water can be raised by means of a suction or bucket pump. This varies in practice according to the efficiency and strength of the pump, but 100 yards is about the maximum for a single lift.

Force pumps can deliver against a much greater " head," and are in more general favour.

Centrifugal and turbo-pumps are, however, rapidly replacing the earlier forms, especially where large quantities of water have to be dealt with.

The Siphon.—If a bent tube be taken with one limb longer than the other, the tube may be used as a siphon tube in the following manner:

Pour water into the tube, and when the shorter limb is full, close it with the finger, and pour water into the longer limb until it, too, is full. Then, holding a finger on each end of the full tube, invert the tube and place the shorter limb under the surface of some water, as in Fig. 32. On removing the fingers, it is now found that water runs out at the end of the longer limb and continues to run out.

The action of the siphon depends upon the atmospheric pressure, and may be explained as follows:

The column of water in *EC* (Fig. 32) exerts a pressure at *C* and, when the siphon begins to work, this water runs out at *C*. As the water proceeds down *EC*, it tends to produce a vacuum in *EA*, and water is consequently drawn from the vessel into the tube. The water now in the tube reaches *E*, runs out at *C*, tends to create the same reduction in pressure in the tube *EA*, and causes more water to be forced from the vessel into the tube as before. The whole process continues, water flowing out steadily at *C*. The reason that the water passes from the vessel into the tube when the vacuum tends to be formed is because of the atmospheric pressure acting on the surface of the water in the vessel.

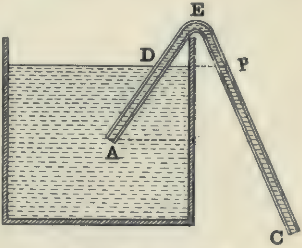


FIG. 32.—SIPHON.

Note.—The water in the tube *ED* exerts a downward pressure at *D* in the same way that the water in *EC* exerts a pres sure at *P*; but the pressure at *C* is greater than that at *D*, because *EC* is longer than *ED;* or, more correctly, because *C* is below the level of the surface of the water in the vessel. It is therefore essential in a siphon that the delivery limb be longer than the other—or, rather, that the end of the delivery limb be below the level of the water to be siphoned. In mining practice water is often conveniently removed from a higher to a lower level by means of a siphon. In such cases the siphon consists of a pipe-line, roughly in the form of an arch, such that the crest of the arch is not more than about 20 feet vertically above the level of the water to be siphoned. This maximum height varies according to the pressure of the atmosphere, but 20 feet may be taken as the maximum under ordinary coal-mining conditions in Britain. At each end of the siphon-pipe is a valve, and at the crest is an opening by which the pipe may be filled with water before use, the valves being closed. This opening also serves as a valve for drawing off any air which may find its way into the siphon and prevent efficient working. The pipe is filled with water and the opening at the top sealed; and, the shorter limb being in the water to be siphoned, the valves at each end are opened—the inlet-end clack valve opening automatically. If the flow of water is too rapid—and it is often desirable to have a slow rate of flow so that the siphon may work continuously day and night—the valve at the delivery end should be closed down until the desired rate of flow is obtained. If, on the other hand, the flow is irregular and uncertain, lengthening the delivery pipe should be tried, which increases the rate of flow. When, however, the delivery end is about 30 feet below the level of the water to be siphoned, further lengthening is of no avail.

In practice it is also advisable to have the delivery end curved upwards a few inches in order to prevent air from finding its way into the siphon.

CHAPTER III

HEAT AND TEMPERATURE.

HEAT is a form of energy. We shall examine this statement more closely later, but at present it is well to bear it in mind.

A red-hot needle is much " hotter " than a bath of warm water. It has therefore a much higher **temperature**; yet it may not contain above a fraction of the heat contained in the warm water. Temperature, then, must be distinguished from heat. **Temperature may be defined as the " hotness " of a body. It is that which governs whether heat will flow from a body to its surroundings or vice versa, heat always flowing from a higher to a lower temperature.**

Measurement of Temperature—Thermometers.—Certain properties of matter vary with the temperature of the matter. Thus the volume of a body increases as the temperature rises, and this fact has been made use of to provide a method for measuring temperatures. The change in volume of a certain quantity of mercury, enclosed in a glass tube, is the most common form in which this method is applied. In order to see the change in volume of the mercury (which change is small) the mercury is caused to expand in a narrow uniform glass tube—called a capillary tube—while the bulk of the mercury is enclosed in a bulb at the end of the tube. When the mercury expands equal distances in the tube, we know there have been equal increases in volume, and we assume that equal increases in volume denote equal increases in temperature. There are two well-known scales for thermometers, the **Fahrenheit** and the **Centigrade.**

The freezing-point of water—or the melting-point of ice—which is the same temperature (see p. 60)—

in the **Fahrenheit** scale is called 32°.
,, **Centigrade** ,, ,, 0°.

Chemical thermometers may be obtained graduated either in Centigrade or Fahrenheit units. The two types of thermometer shown in Figs. 33 and 34 are useful: Fig. 33 showing a chemical thermometer, and Fig. 34 an ordinary room thermometer.

The boiling-point of water at normal pressure—760 mm. (see p. 60)—

is taken on the Fahrenheit scale as 212°.
,, ,, Centigrade ,, 100°.

The intervening space on the Fahrenheit scale is divided into (212 – 32), *i.e.*, 180 equal parts, and each of these corresponds to 1 degree Fahrenheit, or 1° F.

In the Centigrade the intervening space is divided into 100 equal parts, and each corresponds to one degree Centigrade, 1° C. It is evident from above that a range of 180° F. corresponds to a range of 100° C., or that 1° F. corresponds to

$$\frac{100^\circ}{180}\text{ C.} = \frac{5^\circ}{9}\text{ C.}$$

Fig. 33.—Chemical Thermometer (Centigrade).

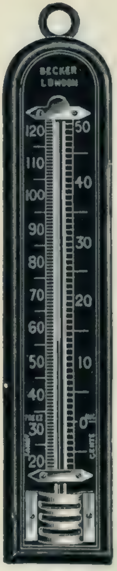


Fig. 34.—Room Thermometer (Fahrenheit).

Now a temperature of –40° F. corresponds with a certain Centigrade temperature, and this can be calculated as follows:

–40° F. is (32 + 40) = 72 degrees Fahrenheit below the freezing-point of water.

Now this range of 72 degrees Fahrenheit corresponds to a range of 72 × $\frac{5}{9}$ degrees Centigrade = 40 degrees Centigrade, and this must be considered below the freezing-point of water.

It is therefore a temperature of −40° C.

I.e., −40° C. = −40° F., and this is the only temperature where the readings of the thermometers are the same.

Based upon this fact is a convenient rule for **converting temperatures in degrees F. to temperatures in degrees C.**

1. **To convert temperatures in °F. to temperatures in °C., add 40, multiply by $\frac{5}{9}$, and then subtract 40.**

2. **To convert temperatures in °C. to temperatures in °F., add 40, multiply by $\frac{9}{5}$, and then subtract 40.**

In either case (1) or (2), first add 40, and finally subtract 40. Whether to multiply by $\frac{5}{9}$ or $\frac{9}{5}$ is easily remembered, when it is borne in mind that the Fahrenheit scale is so much fuller than the Centigrade, and therefore in converting *to* Fahrenheit the factor $\frac{9}{5}$ must be used, whereas in converting *from* Fahrenheit $\frac{5}{9}$ must be used.

E.g.: 1. Convert 60° F., 95° F., 110° F. into °C.

60° F. 60 + 40 = 100 100 × $\frac{5}{9}$ = 55·5 55·5 − 40 = **15·5**° C.
95° F. 95 + 40 = 135 135 × $\frac{5}{9}$ = 75 75 − 40 = **35**° C.
110° F. 110 + 40 = 150 150 × $\frac{5}{9}$ = 83·33 83·33 − 40 = **43·33**° C.

E.g.: 2. Convert 45° C., −30° C., −273° C., 0° C., into °F.

45° C. 45 + 40 = 85 85 × $\frac{9}{5}$ = 153 153 − 40 = **113**° F.
−**30**° C. −30 + 40 = 10 10 × $\frac{9}{5}$ = 18 18 − 40 = −**22**° F.
−**273**° C. −273 + 40 = −233
−233 × $\frac{9}{5}$ = −419·4 −419·4 − 40 = −**459·4**° F.
0° C. 0 + 40 = 40 40 × $\frac{9}{5}$ = 72 72 − 40 = **32**° F.

Quantity of Heat.—The scientific unit of heat is the amount of heat required to raise one gram of water from 4° to 5° C., or for practical purposes through 1° C. It is called the **calorie.**

The **British Thermal Unit,** often used by engineers, is the amount of heat required to raise one pound of water through one degree Fahrenheit (39° to 40° F.). If 10 lbs. of water be raised from 40° to 95° F., the amount of heat required would be $10 \times (95 - 40) = 10 \times 55 = 550$ British Thermal Units.

Similarly, if 15 grams of water be raised from 0° to 30° C., the amount of heat required would be $15 \times 30 = 450$ calories.

Other units of heat are:

The Calorie, which is equal to 1,000 calories.

The Centigrade Heat Unit (C.H.U.), which is the amount of heat required to raise 1 lb. of water 1° C.

When a body cools through a certain range of temperature, it gives out the same amount of heat as was supplied to it to raise it through that range of temperature.

For instance, 15 grams of water cooling from 30° to 0° C. will give out $15 \times 30 = 450$ calories. In general, "m" grams of water cooling through "t"° C. will give out $(m \times t)$ calories; or x lbs. of water cooling through y° F. will give out $(x \times y)$ B.Th.U.

The measurement of quantities of heat is known as **calorimetry.** A calorimeter is a vessel in which the determinations are done. Common calorimeters are merely copper vessels about 6 inches high and 3 inches diameter and open at the top. A few examples will make the subject of calorimetry clear.

E.g.: 1. The heat supplied from 20 grams of water cooling from 50° to 30° C. flows into 10 grams of water at 15° C.

What will the temperature of this water be?

$$\text{Heat given out} = \text{heat taken in}$$
$$20 \times (50 - 30) = 10 \times (t - 15)$$

where t is the final temperature of 10 grams of water.

I.e.,
$$400 = 10(t - 15)$$
$$(t - 15) = \frac{400}{10} = 40$$
$$\therefore \quad t = 40 + 15 = \mathbf{55}° \text{ C.}$$

E.g.: 2. Suppose in the above problem that the two portions of water had been mixed, and the temperature of the mixture were required (the hot water being at 50° C. and the cold at 15° C.).

Let temperature required be $x°$ C.

$$\begin{aligned} \text{Heat given out} &= \text{heat taken in} \\ 20\,(50 - x) &= 10\,(x - 15) \\ 1000 - 20\,x &= 10\,x - 150 \\ 30\,x &= 1150 \\ x &= 38{\cdot}3°\ \text{C.} \end{aligned}$$

Calorimetry is employed to estimate the calorific value of a fuel (see p. 249), and in determinations of specific heats.

Specific Heat.—If equal weights of different substances be taken it is found that they require different amounts of heat to raise them through 1° C. **The quantity of heat required to raise 1 gram of a substance through 1° C. is called its specific heat.**

Thus, 1 gram of copper requires 0·095 calorie to raise its temperature 1° C.; the specific heat of copper is 0·095 calorie per gram degree Centigrade. The specific heats of a few substances are given below.

Water, it will be seen, has a very high specific heat.

TABLE OF SPECIFIC HEATS.

(In calories per gram degree Centigrade.)

Water	= 1·000	Glass	=0·188
Paraffin oil	= 0·683	Iron	=0·113
Alcohol	= 0·615	Copper	=0·095
Ice	= 0·502	Mercury	=0·033
Petrol	= 0·500	Air (constant pressure)	=0·2417
Coal	= 0·241	Air (constant volume)	=0·1715

Consequences of the High Specific Heat of Water.—Practical uses of this fact are seen in the water cooling of air-compressors and engines (especially petrol engines), water condensers for steam, foot warmers, hot-water bottles, etc. If the temperature of water were *readily* raised by a small supply of heat or fell readily by loss of heat, it would be of little use in the above cases.

The **Specific Heat of a Solid** may be found by first weighing the solid and then suspending it from a thread above some water boiling in an open vessel, so that the solid is in steam at atmospheric pressure. After about ten minutes, when the solid has reached the temperature of the steam (100° C.), it is quickly transferred to a weighed copper vessel (calorimeter) in which a certain mass of water at a known temperature is contained. The body is completely immersed and the water stirred well, and the maximum temperature recorded. For very accurate work special types of calorimeter are employed and many precautions are necessary. The following example, however, will make the above method clear:

To find specific heat of a metal (tin):

Weight of metal = 17·27 grams.
Weight of calorimeter (copper) = 33·41 ,,
,, ,, + water (12·6° C.) = 90·05 ,,
∴ Weight of water = 56·64 ,,
Initial temperature of water = 12·6° C.
Final ,, ,, = 14·1° C.

Heat given out by solid = heat taken in by water and by calorimeter.

$$\therefore\ 17{\cdot}27 \times S \times (100^\circ - 14{\cdot}1^\circ) = [56{\cdot}64 \times (14{\cdot}1 - 12{\cdot}6)] + [33{\cdot}41 \times 0{\cdot}095 \times (14{\cdot}1 - 12{\cdot}6)]$$

where S = specific heat of the metal.

I.e., $17{\cdot}27 \times S \times 85{\cdot}9 = (56{\cdot}64 \times 1{\cdot}5) + (33{\cdot}41 \times 0{\cdot}095 \times 1{\cdot}5)$.

Hence S = 0·060 calories per gram °C.

[Correct result = (0·056).]

The Specific Heat of a Liquid may be found similarly by mixing a known mass of the liquid heated to a certain temperature with a known mass of cold water in a calorimeter, and noting the rise in temperature.

Specific Heats of a Gas.—When gases are heated or cooled, they expand or contract to a very considerable extent (see p. 53). The amount of heat given out by a certain mass of gas in cooling through 1° C. is, of course, the same as the amount of heat required to raise that mass of gas through 1° C., provided the conditions of heating and cooling are the same.

Now, in heating a gas, the expansion may be allowed to take place by artificially increasing the size of the vessel according as the gas expands; or, the vessel may be of fixed definite size, so that, instead of the gas expanding, it merely increases its pressure on the walls of the containing vessel. In the first case there is no increase in pressure but an increase in volume; in the second case there *is* an increase in pressure but no increase in volume. It is possible, therefore, to find for every gas two specific heats: (1) C_p, or the specific heat at constant pressure; (2) C_v, or the specific heat at constant volume. Moreover, C_p is always greater than C_v, as by compressing a gas (which takes place in heating a gas and maintaining its volume constant) the gas *of itself* becomes hot, or, in other words, heat is developed. (This is known by all who use a bicycle pump.) Such heat is "internal" heat, and assists the "external" heat applied to warm the gas. Less heat will therefore be required to raise a given mass of gas through a certain range of temperature if the gas is not allowed to expand than would be required if the gas *were* allowed to expand. In other words, C_v is less than C_p. The values of C_p and C_v are important to scientists and engineers, but their application is beyond the scope of this book.

Expansion of Solids.—One general effect of heat on matter is to cause it to expand or increase in volume. This is true whether the matter be in the solid, liquid, or gaseous state.

Different bodies expand at different rates. Experiments prove that if a rod of a certain length be taken at 0° C., then for each degree Centigrade which the temperature is raised the rod will add on a definite fraction of its length at 0° C., and this fraction is called the **coefficient of linear expansion** of the material per degree Centigrade.

The coefficient of linear expansion of steel is 0·000012 per degree Centigrade. It follows that a steel rod 1 yard long at 0° C. is—

At 1° C.	1·000012	yards.
,, 10° C.	1·00012	,,
,, 15° C.	1·00018	,,

Similarly, a steel rod 1 cm. long at 0° C. will be—

At 1° C.	1·000012 cm.
,, 10° C.	1·00012 ,,
,, 15° C.	1·00018 ,,

In symbols, if L is the length of the rod at 0° C. and α is the coefficient of linear expansion of the material, then the length at any temperature t° C. is—

$$L\,(1+\alpha\,.\,t).$$

For general calculations, as the length at 0° C. is very little different from that at ordinary temperatures, L is often regarded as this latter length. This, of course, is not strictly correct, but the error is negligible for most purposes.

To Find the Coefficient of Linear Expansion of a Solid.—In order to obtain rapid and uniform heating, a thin rod *AB* of the material is taken. This is supported on corks inside a large (jacket) tube *C* which has two outlets *E* and *F*.

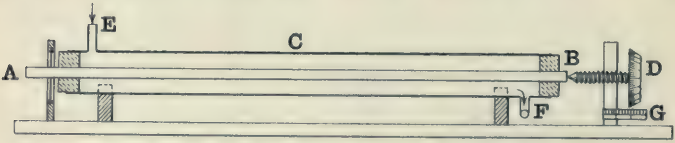


FIG. 35.

One end *A* of the rod is fastened (as near as possible to the cork) between two knife-edges, and the other end *B* just projects beyond the other cork. The screw *D*, whose pitch is known, has its head divided into 100 equal parts so that fractions of a turn may be read. (This arrangement is common on screw-gauges, spherometers, and the like.) If the pitch is 1 mm., one of these divisions of the head corresponds to 0·01 mm.

The screw is first set well away from the end *B*. Steam is passed through the jacket tube until no further expansion of the inner tube is noted. A thermometer (not shown) is placed with its bulb in *C* and registers the temperature. Screw *D* is now adjusted till it just touches the end B of the rod, and the reading on G and on the screw-head is noted. The steam is now turned off, and cold water is sent through the jacket tube, C, causing contraction. After a while screw D is again adjusted to B, the reading taken, and the temperature noted. The length of the rod between the knife-edge mark and the end B is then measured, and the coefficient of linear expansion calculated as follows. *E.g.*, a copper rod was taken: Length 100 cm.; initial (steam) temperature = 100° C.; final (water) temperature = 15° C.; initial reading on scale G, etc. = 5·231 cm.; final reading on scale G, etc. = 5·081 cm.; expansion = 5·231 − 5·081 = 0·150 cm.; change of temperature = 85° C.

∴ Coefficient of expansion of copper

$$= \frac{0{\cdot}15}{100 \times 85} = 0{\cdot}0000177 \text{ per } ^\circ\text{C.}$$

COEFFICIENTS OF LINEAR EXPANSION (PER °C.).

Copper	= 0·0000172	Glass	= 0·0000084
Iron (soft)	= 0·0000122	Platinum	= 0·0000084
Steel	= 0·0000108	Ebonite	= 0·0000770
Aluminium	= 0·0000222	Zinc	= 0·0000290

The coefficient of expansion (linear, superficial, or cubical) of any material per °C. may be converted to the coefficient of expansion per °F. by multiplying by $\frac{5}{9}$.

Examples: 1. In a survey the base line is to be 3 miles long and laid out by an iron chain whose length is correct at 0° C. If the average temperature is 17° C., find the error in length if the expansion of the iron is neglected. Take the coefficient of expansion of iron as 0·000012 per °C.

$$3 \text{ miles} = 3 \times 5280 \text{ feet.}$$
$$3 \times 5280 \times 0{\cdot}000012 \times 17 = \mathbf{3{\cdot}23 \text{ feet.}}$$

2. If it takes a force of 130 tons per square inch to produce a 1 per cent. diminution in the length of an iron bar, what force will be required to prevent an iron bar 3 inches long and of section 1 inch square from expanding lengthways when heated from 0° to 500° C? (Coefficient of expansion of iron = 0·000012 per °C.)

If unimpeded, the length of the bar would be—

$$\begin{aligned}&3+(3\times 0{\cdot}000012\times 500) \text{ inches}\\ &=3+0{\cdot}018\\ &=3{\cdot}018 \text{ inches.}\end{aligned}$$

Now an increase of $\frac{3}{100}$ of an inch would, if prevented, require a force of 130 tons.

$\therefore$ An increase of 0·018 inch requires $130\times\frac{0{\cdot}018}{0{\cdot}03}=$ **78 tons.**

Superficial Expansion of Solids.—That fraction of its area at 0° C. by which the area of a solid increases for 1° C. rise in temperature is known as the coefficient of superficial expansion of the solid. This can be shown to be approximately double the coefficient of linear expansion as follows:

Imagine a square of material 1 inch edge at 0° C., and let the coefficient of linear expansion be α.

Then at 1° C. the length of each side of the square will be $(1+\alpha)$ inch and the new area $(1+\alpha)^2$ square inches.

Now the original area was 1 square inch.

$$\begin{aligned}\therefore \text{ The increase in area} &=(1+\alpha)^2-1 \text{ square inch}\\ &=1+2\alpha+\alpha^2-1 \quad ,, \quad ,,\\ &=2\alpha+\alpha^2.\end{aligned}$$

Now α being very small α^2 is negligible.

$$[(\tfrac{1}{1000})^2=\tfrac{1}{1000000}, \text{ or } (0{\cdot}001)^2=0{\cdot}000001.]$$

$\therefore$ The increase in area is 2α, which is twice the increase in length, or the **coefficient of superficial expansion is twice the coefficient of linear expansion.**

Cubical Expansion of Solids.—That fraction of its volume at 0° C. by which the volume of solid increases for 1° C. rise in temperature is called the coefficient of cubical expansion of the solid.

A cube whose edge is 1 inch long at 0° C. will have at 1° C. an edge of $(1+\alpha)$ where α is the coefficient of linear expansion as before.

The volume of the cube will be $(1+\alpha)^3$ and the increase in volume will be $(1+\alpha)^3-1^3$

$$\begin{aligned}&=1+3\alpha+3\alpha^2+\alpha^3-1\\&=3\alpha+3\alpha^2+\alpha^3.\end{aligned}$$

The terms in the above expression containing $\alpha^2+\alpha^3$ are so small as to be negligible, as before.

It follows that the increase in volume is 3α; or **the coefficient of cubical expansion of a solid is three times the coefficient of linear expansion.**

Applications.—The force of expansion or contraction is enormous, and has to be allowed for in practical construction.

In colliery work special expansion joints are provided on steam-pipes. These joints may take the form of a loop of piping which is somewhat flexible, or a short section of corrugated metal may be inserted in the pipe-line; or, again, a stuffing-box arrangement may be used (Fig. 36). The walls of houses which have been seriously affected by subsidence of the ground may be drawn together and held in position by passing through them iron bars, which are tightened while hot, and allowed still further to tighten as they are contracting.

Spaces are left between lengths of rail on a railway to allow for the expansion in the warm weather. Rivets gain much of their usefulness from the contraction which they undergo on cooling. Iron bands on cart-wheels are put on hot and allowed to cool and contract, and thus bind the wooden sections firmly together.

It is interesting to note it is largely because platinum and glass have the same coefficient of expansion that it is possible to fuse platinum wires into glass tubes. This has been of considerable assistance in carrying out many scientific experiments.

Expansion of Liquids.—When liquids expand an allowance for the expansion of the containing vessel must be made in measuring the expansion of the liquid. The observed expansion of the liquid is called the "apparent expansion." The "real expansion" of the liquid is greater than this by the expansion of the containing vessel or, real expansion = apparent expansion + expansion of vessel. Different liquids expand at different rates. The coefficient of expansion of a liquid is that fraction of its *volume* at 0° C. which a liquid expands on being heated to 1° C.

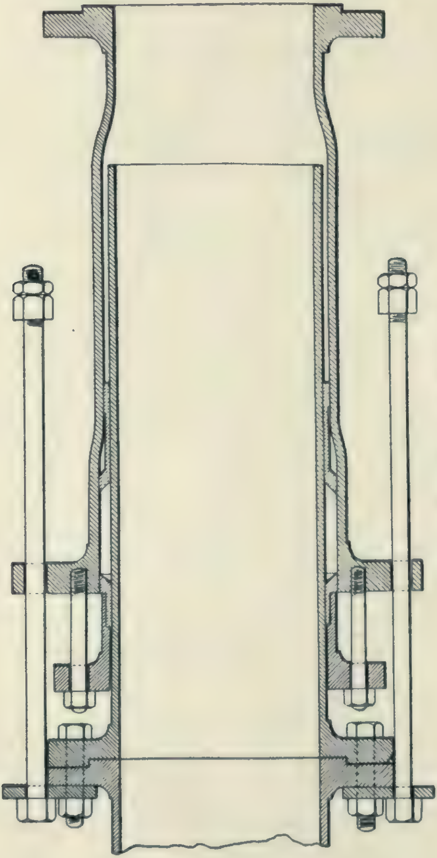


FIG. 36.—EXPANSION JOINT.

E.g.: 1. 1,000 c.c. of a liquid are heated from 0° to 50° C.

The coefficient of expansion of the liquid is 0·00108. Find the volume at 50° C.

Amount of expansion $= 1000 \times 0{\cdot}00108 \times 50 = 54$ c.c.

$\therefore$ Volume at 50° C. $= 1000 + 54 = 1054$ c.c.

As the volumes of both solids and liquids vary with changes of temperature, it is obvious that their densities likewise vary. Density $= \frac{\text{mass}}{\text{volume}}$. The mass is constant at all temperatures, but with rise of temperature the volume generally increases. It follows that at higher temperatures the density of a substance is less than at lower temperatures.

E.g.: 2. In the above example, let the mass of the liquid be 800 grams.

Find the density at 0° C. and at 50° C.

$$\text{Density at } 0^\circ \text{ C.} = \frac{800}{1000} = 0{\cdot}800 \text{ gram per c.c.}$$

$$\text{,, \quad ,, \quad } 50^\circ \text{ C.} = \frac{800}{1054} = 0{\cdot}759 \text{ \quad ,, \quad ,,}$$

Water has a density in grams per cubic centimetre at

4° C. of 1·0000
10° C. ,, 0·9997
20° C. ,, 0·9982
30° C. ,, 0·9957

COEFFICIENTS OF EXPANSION OF SOME LIQUIDS.

Per Degree Centigrade.

Water	0·00012 at 15° C. to 0·00074 at 90° C.
Alcohol	0·00108
Mercury	0·000182
Petroleum ..	0·00104

The above figures are for ordinary temperatures.

Note.—Due partly to the great difference between the coefficients of expansion of mineral oil and water, the oil separates readily from any water which it contains if the mixture be warmed.

Expansion of Water.—The behaviour of water at low temperatures when heated is exceptional. *Water* at 0° C. (32° F.) on being heated does not expand but contracts until a temperature of 4° C. (39° F.) is reached. Above this temperature it expands on heating, as does any other liquid. 4° C. is then the temperature of maximum density of water, or, in other words, more matter is contained in a certain volume of water at that temperature than is contained by the same volume of water at any other temperature. (It will be remembered that 1 gram is the mass of 1 c.c. of water at 4° C.)

Hope's experiment verifies the above maximum density temperature.

In this experiment a tall metal cylinder (Fig. 37) full of water at about 10° C. (50° F.) is taken and the middle part of the cylinder is surrounded by a mixture of ice and salt in order to cool down the water inside the cylinder and eventually freeze it. Two thermometers are so placed that the temperatures of the water at the top and the bottom of the cylinder can be read.

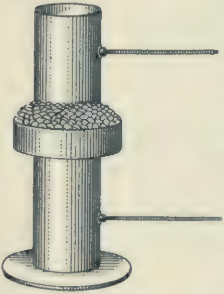


FIG. 37.—HOPE'S APPARATUS.

Results.—The lower thermometer is the first to show the effect of cooling, and the mercury drops gradually to 4° C., where it remains stationary to the end of the experiment.

Shortly after the bottom thermometer has reached the temperature of 4° C. the mercury in the top thermometer begins to drop fairly quickly and eventually reaches 0° C., when ice begins to form at the surface.

Explanation.—The water nearest to the freezing mixture of ice and salt is the first to be cooled. It contracts in volume or becomes heavier bulk for bulk than the surrounding water (*i.e.*, denser), sinks to the bottom, and lowers the temperature of the bottom thermometer. This continues until a temperature of 4° C. is reached in the lower half of the cylinder. On further cooling the water nearest the freezing mixture becomes less dense and rises, lowers the temperature of the top thermometer, and continues to lower it until the water freezes at 0° C. at the top.

It is on account of this fact that water always freezes at the surface while the liquid underneath (which can only be cooled very slowly by conduction) remains at a temperature of about 4° C. Fishes are thus able to survive through the cold season. (Had the behaviour of water in this respect been different, it is interesting to reflect on the changes that might have occurred in evolution.) In other words, in the cooling down of water from 10° C. (say) it contracts in volume until a temperature of 4° C. is reached, but, on cooling further, it expands and, when the freezing-point is reached and the water changes to ice, the expansion is considerable. Ten volumes of water at 0° C. become 11 volumes of ice, and it is this expansion that causes the bursting of pipes, etc., in the frosty weather, though it is usually only when the thaw sets in that the leak attracts attention and the burst is observed.

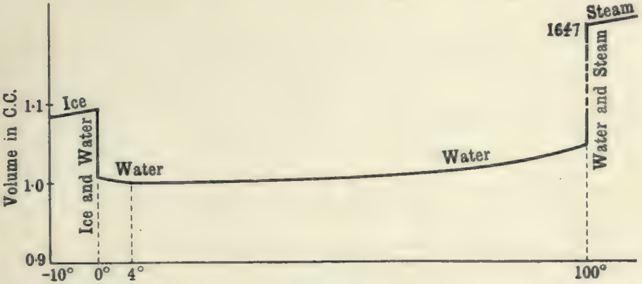


Fig. 38.

The changes in volume which water undergoes when heated are indicated graphically in Fig. 38. The alteration in volume when water changes to steam at 100° C. is enormous, and only roughly suggested in the graph. Observe that the temperature is constant where change of state occurs—*i.e.*, where ice becomes water and where water becomes steam.

CHAPTER IV

Expansion of Gases.

Effect of Pressure.—Experiment to determine the relation between the pressure and volume of a given mass of gas.

Take a stout glass U-tube with one limb of known cross-sectional area, shorter in length than the other limb, and sealed. Pour mercury down the open limb until the mercury column entraps a certain amount of air in the short limb, and add a little more mercury. Now the entrapped air is under pressure. In the first place there is the atmospheric pressure acting on the surface *AB* and transmitted through the mercury to the enclosed gas. In the second place there is, in addition, the pressure of the column of mercury between *CD* and *AB* whose height is denoted by h. Now, if the limbs of the U-tube be graduated (in centimetres and tenths of centimetres say), the volume of gas enclosed can be read off, and also the height, h, of the mercury column. Add more mercury in the open tube. The height, h, will increase and the volume of gas decrease. By this means a number of values for the volume of the gas and the corresponding pressure can be obtained.

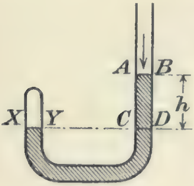


Fig. 39.

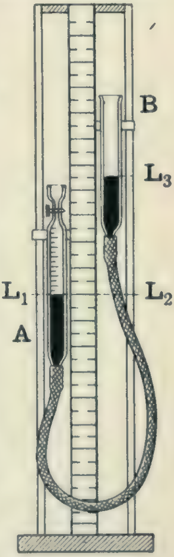


Fig. 40.—Boyle's Law Apparatus.

A more convenient form of apparatus, however, is shown in Fig. 40.

A is connected to *B* by stout rubber tubing. The adjustable vessel *B*, containing mercury, serves as a convenient method of increasing or decreasing the pressure. The tap of vessel *A* is maintained closed throughout the experiment after the air has been introduced at the start. The difference in level between L_3 and L_2 is read off direct on the scale provided. Having obtained six or seven readings for volumes and corresponding pressures, tabulate as follows:

I. Volume in c.c.	II. $L_3 - L_2$ Pressure in mm.	III. Barometric pressure in mm.	IV. II + III Total pressure in mm.	V. I × IV Volume × Pressure

The values found for column V. should be very nearly constant. Plot the results on a graph, taking volumes as abscissæ (*i.e.*, on the horizontal scale).

This form of graph (Fig. 41) is known as an hyperbola, or as a hyperbolic curve. It is a very important type for engineers as it is the curve obtained when the pressures and volumes of expanding steam are plotted. This is done mechanically in the **indicator diagram,** where the area enclosed by the curve corresponds to the work done by the steam on the piston of the engine. In the Indicator Diagram (Fig. 42) only the upper, right-hand part of the diagram is occupied by the curve showing the expansion of steam. From the above results it

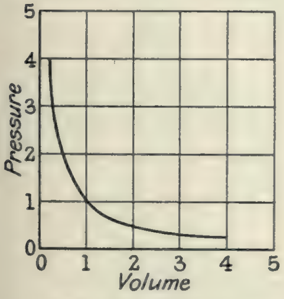


FIG. 41.—HYPERBOLA.

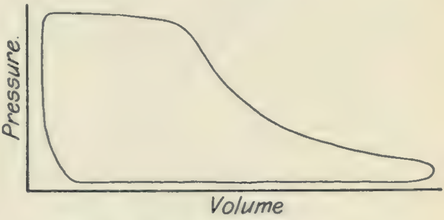


FIG. 42.—INDICATOR DIAGRAM.

will be seen that the pressure × volume is apparently constant throughout. In other words, the pressure varies inversely as the volume. This law is approximately true for all gases, and is known as **Boyle's Law.** In symbols

$$P \propto \frac{1}{V} \text{ or } P_1 \times V_1 = P_2 \times V_2 = k.$$

It is important to note that throughout the above experiments the temperature is constant. If the temperature varies during the experiment the results obtained will not indicate the law stated.

The **theory of gas pressure** may be mentioned here. Any gas enclosed in a space exerts a pressure on the sides of the containing vessel. This pressure is the result of the bombardment on the sides of the vessel by the minute particles or molecules of the gas. The molecules are flying about in all directions with enormous velocities, and they are supposed to be perfectly elastic so that they rebound from their collisions (with one another and with the walls of the vessel) with the same velocity as they had before colliding. If the volume of the vessel be increased, the rate of bombardment will be smaller, the molecules having so much farther to travel before hitting a wall and rebounding to hit another wall, and the pressure on the sides of the vessel is decreased. On the other hand, if the volume of the vessel be decreased (without, of course, allowing any gas to escape) the bombardment is more intense; there is, as it were, a massed attack, a concentration of forces, and the pressure rises in proportion.

It was Robert Boyle who first stated the exact relation of the pressure to the volume of a certain mass of gas. He found that if the pressure were doubled the volume was halved; that if the pressure were made five times as great the volume was reduced to one-fifth; that if the pressure were reduced to one-quarter, the volume was increased to four times; and so on. In other words, **the volume of a given mass of gas varies inversely as the pressure to which it is subjected.** This, however, it must be remembered, is only true provided that the temperature is constant.

E.g., what volume will 500 cubic feet of air at a pressure denoted by 29 inches of mercury column occupy if the barometer rises to 30·5 inches, the temperature being constant?

$$P_1 \times V_1 = P_2 \times V_2$$
$$29 \times 500 = 30{\cdot}5 \times V_2$$
$$V_2 = \frac{29 \times 500}{30{\cdot}5} = 475{\cdot}4 \text{ cubic feet.}$$

Temperature and Volume of a Gas.—In considering the effects of a change of temperature on the volume of a given mass of gas it is necessary to keep the pressure constant, just as in considering the relations between pressure and volume the temperature is maintained constant.

It is found that if gases be heated and the pressure adjusted so as always to be constant:

(*a*) **All gases expand at the same rate.**

(*b*) **The volume of a gas increases by $\frac{1}{273}$ of its volume at 0° C. for each degree Centigrade rise in temperature.**

This is known as **Charles' Law.**

In symbols the volume V_t of a given mass of gas at a temperature of t° C. is

$$V_t = V_o \left(1 + \frac{t}{273}\right)$$

where V_o is the volume of the gas at 0° C. *E.g.*, find the volume of a gas at 54·6° C. if its volume at 0° C. is 3·25 cubic feet.

$$V_t = V_o \left(1 + \frac{t}{273}\right)$$
$$= 3{\cdot}25 \left(1 + \frac{54{\cdot}6}{273}\right)$$
$$= 3{\cdot}25 \ (1 + 0{\cdot}2) = 3{\cdot}25 \ (1{\cdot}2)$$
$$= 3{\cdot}90 \text{ cubic feet.}$$

If the Fahrenheit scale be employed, Charles' Law may then be stated that **the volume of a gas increases by $\frac{1}{459}$ of its volume at 0° F. for each degree F. rise in temperature,** or

$$V_t = V_o \left(1 + \frac{t}{459}\right).$$

It will be seen that at a temperature of −459° F. or −273° C. the volume of any quantity of gas would become zero according to the above. However, all gases liquefy before they reach this temperature, and, having thus ceased to be gases, they no longer follow the law.

The temperature of −273° C. or −459° F. is called the **absolute zero.** We may thus draw up four thermometric scales (Fig. 43).

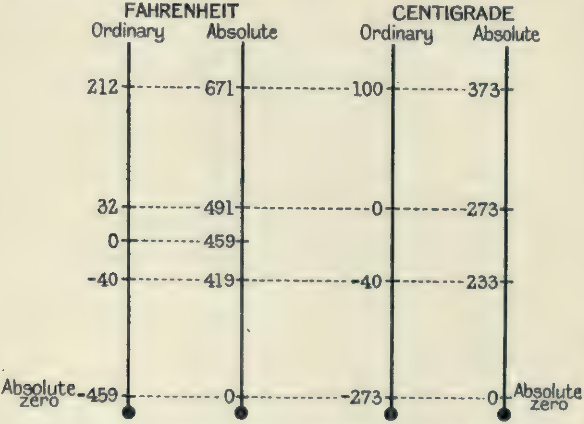


FIG. 43.—COMPARISON OF TEMPERATURE SCALES.

Thus a temperature of 10° C. or 50° F. may be expressed as 283° C. (absolute), or as 509° F. (absolute).

Now 273 cubic feet of gas at 0° C. or 273° C. absolute
become 274 ,, ,, ,, 1° C. ,, 274° C. ,,
or become 283 ,, ,, ,, 10° C. ,, 283° C. ,,
,, 263 ,, ,, ,, −10° C. ,, 263° C. ,,

Charles' Law may therefore be stated thus: **The volume of a given mass of gas is proportional to its absolute temperature, provided the pressure is constant.**

In symbols $V \propto T$, where T is the absolute temperature, or

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}=\frac{V_3}{T_3}=k.$$

E.g.: 1. 10 cubic feet of a gas at 87° F. are cooled down to a temperature of 41° F., the pressure being constant. What is the volume at 41° F.?

$$87^\circ \text{ F.} = (87+459)^\circ \text{ F. abs.} = 546^\circ \text{ F. abs.}$$
$$41^\circ \text{ F.} = (41+459)^\circ \text{ F. ,,} = 500^\circ \text{ F. ,,}$$

Now, according to Charles' Law—

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

i.e.,

$$\frac{10}{546} = \frac{V_2}{500}$$

whence

$$V_2 = \frac{10 \times 500}{546} = 9{\cdot}16 \text{ cubic feet.}$$

E.g.: 2. 40,000 cubic feet of air per minute are passing down a shaft at 10° C. and are heated in the workings of the mine to 20° C. What volume of air per minute would come out of the mine if the pressure were constant?

$$10^\circ \text{ C.} = 283^\circ \text{ C. absolute.}$$
$$20^\circ \text{ C.} = 293^\circ \text{ C. ,,}$$
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$\frac{40000}{283} = \frac{V_2}{293}.$$
$$\therefore V_2 = \frac{40000 \times 293}{283}$$
$$= 41413 \text{ cubic feet.}$$

E.g.: 3. Suppose in *E.g.* 2 above the pressure had changed from 30·5 inches mercury in the downcast to 30 inches mercury in the upcast, what would then have been the volume of air per minute coming out of the mine?

If there had been no change in pressure, we have seen that the volume would have been 41,413 cubic feet. It is therefore simply a question of what volume 41,413 cubic feet of air at a pressure of 30·5 inches mercury column will occupy when the pressure drops to 30 inches mercury column.

By Boyle's Law—

$$P_1 \times V_1 = P_2 \times V_2$$
$$30{\cdot}5 \times 41413 = 30 \times V_2$$
$$V_2 = \frac{41413 \times 30{\cdot}5}{30}$$
$$= 42103 \text{ cubic feet.}$$

E.g.: 4. A goaf has a volume of 1,000 cubic yards filled with air and various other gases. The temperature is 70° F., and the barometric pressure is 30·3 inches mercury. The pressure then falls to 29·1 inches mercury, and "heating" in the "waste" increases the temperature to 91° F. What volume of gases escapes from the waste ?

Consider first the effect of temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$\frac{1000}{459+70} = \frac{V_2}{459+91}$$
$$\frac{1000}{529} = \frac{V_2}{550}$$
$$V_2 = \frac{550 \times 1000}{529} \text{ cubic yards.}$$

This is what the volume would have been if the temperature only had changed. The pressure, however, has also changed. And the question now becomes, "What volume will $\left(\frac{550 \times 1000}{529}\right)$ cubic yards of gas at 30·3 inches barometer occupy at 29·1 inches ?"

From Boyle's Law—

$$P_1 \times V_1 = P_2 \times V_2$$
$$30{\cdot}3 \times \frac{550 \times 1000}{529} = 29{\cdot}1 \times V_2$$

whence

$$V_2 = \frac{30{\cdot}3 \times 550 \times 1000}{29{\cdot}1 \times 529}$$
$$= 1082{\cdot}6 \text{ cubic yards.}$$

∴ The volume which has escaped is 82·6 cubic yards or 2,230 cubic feet.

E.g. 5. In *E.g.* 4 above calculate the density in lbs. per cubic foot of the warmer gaseous mixture if the density of the gaseous mixture at 70° F. and 30·3 inches barometer is 0·070 lb. per cubic foot.

$$\text{Mass of the mixture} = 1000 \times 27 \times 0{\cdot}07 \text{ lbs.}$$
$$= 1890 \text{ lbs.}$$

This mass is, of course, constant throughout. When the gaseous mixture is warm, therefore 1,890 lbs. occupy a volume of $1082{\cdot}6 \times 27$ cubic feet.

The density of the warmer mixture is therefore

$$\frac{1890}{1082{\cdot}6 \times 27} \text{ or } \frac{1000 \times 27 \times 0{\cdot}07}{1082{\cdot}6 \times 27} = 0{\cdot}0647 \text{ lb. per cubic foot.}$$

It should, from this example, be clear that the density of a given mass of gas varies inversely as its volume. This statement is true from the very definition of density as $\frac{\text{mass}}{\text{volume}}$, but the point is apt to be overlooked because of the fact that the volume of a solid or a liquid is subject only to slight, often inappreciable, changes by alterations of temperature and pressure. In the case of a gas, changes of temperature and pressure produce very marked changes in volume, and therefore in density.

Density of Air.—One cubic foot of air at 0° C. and at a barometric pressure of 30 inches of mercury weighs 0·0807 lb. In other words, the density of air at N.T.P. (normal temperature and pressure—*i.e.*, 0° C. and 30 inches barometer or 760 mm. barometer) is 0·0807 lb. per cubic foot.

If the barometer be reduced to 1 inch mercury, the volume of the original 1 cubic foot would be 30 cubic feet, the temperature being constant.

The density of the air would therefore be $\frac{0{\cdot}0807}{30}$ lb. per cubic foot $= 0{\cdot}00269$ lb. per cubic foot.

Similarly, if the barometer were 20 inches, the density of the air would be $\frac{0{\cdot}0807}{30} \times 20$ lb. per cubic foot, or $20 \times 0{\cdot}00269$ lb. per cubic foot.

In general, if the temperature is maintained constant at 0° C., the weight of 1 cubic foot of air at a barometric pressure of B inches of mercury is given by $(0{\cdot}00269 \times \mathrm{B})$ lb.

The effect of temperature may be seen as follows:

Suppose the barometer constant at 1 inch mercury, and the temperature of the air is changed from 0° to 1° C. The volume of 1 cubic foot at 0° C. then becomes, by Charles' Law $(1 + \frac{1}{273})$ cubic feet. One cubic foot of this air at 1° C. will therefore weigh $\frac{0{\cdot}00269}{\left(1 + \frac{1}{273}\right)}$ lb.

If the temperature be raised to 2° C., the weight of 1 cubic foot of the air then becomes $\frac{0{\cdot}00269}{\left(1 + \frac{2}{273}\right)}$ lb., and at t° C. the weight of 1 cubic foot of air is $\frac{0{\cdot}00269}{\left(1 + \frac{t}{273}\right)}$ lb., which may be expressed as $\left(\frac{0{\cdot}00269 \times 273}{273 + t}\right)$ lb. or as $\left(\frac{0{\cdot}7344}{273 + t}\right)$ lb.

This gives the weight of 1 cubic foot of air at any temperature "t" and under a barometric pressure of 1 inch mercury. At any barometric pressure B inches of mercury and temperature t° C., the **weight of 1 cubic foot of air is given by the expression** $\left(\frac{0{\cdot}7344 \times \mathrm{B}}{273 + t}\right)$ lb.

If the barometer is given in millimetres the weight of 1 cubic foot of air is then $\left(\frac{0{\cdot}7344 \times \frac{\mathrm{B}}{25{\cdot}4}}{273 + t}\right)$ lb., as there are 25·4 mm. in 1 inch.

If the Fahrenheit scale of temperature is employed, the above expressions become modified, due to the fact that a gas expands only $\frac{1}{459}$ of its volume at 0° F. for each degree Fahrenheit rise in temperature. The expression for the

weight of a cubic foot of air at any temperature f° F., and at any pressure B inches of mercury then becomes—

$$\left(\frac{1{\cdot}3253 \times \mathrm{B}}{459 + f}\right) \text{lb.}$$

The laws connecting the volume of a gas with the pressure and temperature are of great importance in ventilation problems. They also are of service in calculations on compressed air; and, though at this stage we cannot enter into the more advanced physics of air-compression, the following example should be easily within the student's grasp.

E.g.: 1. Twenty cubic feet of "free" air at 15° C. are compressed to a gauge pressure of 100 lbs. per square inch. If the temperature rises to 27° C., what is the volume of the compressed air ? Assume the atmospheric pressure to be 15 lbs. per square inch.

If there had been no rise in temperature the volume V_2 of the compressed air would have been obtained thus—

$$P_1V_1 = P_2V_2$$

$$15 \times 20 = 115 \times V_2$$

whence $$V_2 = \frac{15 \times 20}{115} = 2{\cdot}609 \text{ cubic feet.}$$

This volume of gas, however, has its temperature raised from 15° C. to 27° C. The volume therefore becomes—

$$2{\cdot}609 \times \frac{273 + 27}{273 + 15} = 2{\cdot}718 \text{ cubic feet.}$$

Change of State and Latent Heat.

There are three states of matter—the solid, the liquid, and the gaseous. Before a substance will pass from one of these states to another, two conditions must be fulfilled:

1. **The substance must come to a definite temperature.**
2. **Heat must be supplied to or taken from the substance according to the direction in which the change is going.**

Thus, heat must be supplied to change a solid to a liquid or a liquid to a gas (*e.g.*, ice to water, and water to steam), but heat must be removed or abstracted to turn a gas to a liquid or a liquid to a solid (*e.g.*, steam to water and water to ice).

Now, whenever change of state occurs, the whole change takes place at a fixed temperature. Ice at 0° C. turns to water at 0° C., and similarly if water at 100° C. turns to steam, the steam is at 100° C., unless, of course, it is subsequently (super-)heated. Nevertheless, during these changes of state it is necessary continuously to supply heat, and this heat, which produces change of state but does not alter the temperature, is known as **latent heat,** or " hidden heat."

The heat that must be supplied to 1 gram of a substance to change it from the solid state to the liquid state without altering its temperature is called the **Latent Heat of Fusion** of the substance. It requires 80 calories to convert 1 gram of ice at 0° C. into 1 gram of water at 0° C.; and, similarly, 1 gram of water at 0° C. gives out 80 calories in turning to ice at 0° C.

The **Latent Heat of Fusion of Ice** is, therefore, 80 calories per gram, or in engineering units 144 B.Th.U. per lb. The heat that must be supplied to 1 gram of a substance to change it from the liquid to the gaseous state is termed the **Latent Heat of Vaporisation** of the substance. It requires 537 calories to convert 1 gram of water at 100° C. into steam at 100° C.; and this heat is likewise emitted by 1 gram of steam at 100° C. condensing to water at 100° C. **The Latent Heat of Vaporisation of Water is therefore 537 calories per gram, or in engineering units 966 B.Th.U. per lb.**

Effect of Pressure upon the Temperature at which Change of State Occurs.—Pressure can effect a change in the melting- and the boiling-points of a substance owing to the change in volume which takes place on change of state. In the cases of solids turning to liquids (or *vice versa*) the change in volume is small, and consequently the effect of pressure on the temperature of melting (or solidification) is also small. When water freezes it expands; when ice melts it contracts. Increase of pressure therefore assists melting since it assists contraction, and consequently the ice melts under increased pressure at temperatures below 0° C. On the other hand, increase in pressure tends to prevent expansion and therefore retards freezing. In consequence, water will not freeze even below 0° C. under increased pressure. Glaciers travelling down mountain slopes and valleys thaw at those places where the pressure is greatest (even though the temperature be well below 0° C.), such as at the base and sides, especially when moving over rough ground or travelling along a winding course.

In the case of a liquid turning to a vapour, the change in volume is frequently enormous. Thus, 1 cubic foot of water at 100° C. forms about 1,650 cubic feet of steam at the same temperature. Now this expansion has to take place against whatever pressure is acting on the water at the time. If this pressure is small, the change to steam will take place more readily (*i.e.*, at a lower temperature) than if the pressure is large. Increase of pressure therefore tends to raise the boiling-point. Decrease of pressure, on the other hand, lowers the boiling-point. In fact, by gradually reducing the pressure the boiling-point may be lowered step by step until the water boils at 0° C. It is only when the pressure of the atmosphere is equal to 760 mm. (or 30 inches) of mercury column that water boils at exactly 100° C. Should the barometer be higher, the temperature of boiling will be higher, and *vice versa*.

In a boiler generating steam at a gauge pressure of 80 lbs. per square inch the water boils not at 100° C. (212° F.), but at 162° C. (324° F.). The gauge pressure gives the difference between the atmospheric pressure and the pressure inside the boiler. The total or absolute pressure is therefore $(80 + 15 =)$ 95 lbs. per square inch.

Boiling should be distinguished from evaporation. The boiling-point of a liquid is that temperature at which the liquid **turns to the gaseous state not only at its surface but from all parts.**

Evaporation, however, is the **conversion of a liquid only at its surface into the gaseous state** (see p. 75). It is convenient here to note that substances dissolved in the water raise the boiling-point and lower the freezing-point. It is on account of this lowering of the freezing-point that calcium chloride is sometimes dissolved in the water used for cooling the radiator of a motor-car. The low temperature required to freeze such a solution is hardly ever reached in a temperate climate, and troubles arising from bursting of the radiator-tubes, etc., are avoided. But the possibility of the chemical action of such solutions on the metals with which they come into contact must be borne in mind.

It has been seen how the temperature of change of state may vary. The Latent Heat of Vaporisation of Steam varies with the temperature (which depends upon the pressure) at which change of state occurs. This Latent Heat, L, in B.Th.U. at any temperature t° F. may be found by **Regnault's Formula:**

$$L = 966 - 0{\cdot}7\,(t - 212);$$

or

$$L = 966 - 0{\cdot}7t + 148{\cdot}4;$$

or

$$L = (1114 - 0{\cdot}7t)\ \text{B.Th.U.}$$

E.g., water is fed into a boiler at 52° F. and is completely vaporised at 300° F. Find the total heat given to each pound of water.

The total heat is made up of:

(*a*) The heat required to raise the temperature;
(*b*) ,, ,, effect change of state.

The heat required to raise 1 lb. of water from 52° to 300° F. is (300 − 52) B.Th.U. = 248 B.Th.U.

The heat required to effect change of state will be from the above formula:

$$1114 - (0{\cdot}7 \times 300)\ \text{B.Th.U.}$$
$$= 904\ \text{B.Th.U.}$$

Total heat supplied to each pound of water, therefore, is (248 + 904) = **1152 B.Th.U.**

Calorific Power or Calorific Value of a Fuel.—The heating value of a fuel is *sometimes* indicated by giving the number of pounds of water at 212° F. (or 100° C.) which 1 lb. of the fuel could turn to steam at 212° F. if all the heat given out were employed in heating the water. To convert such a value—called the **evaporative value**—into calories per gram it is necessary to multiply by 537. To convert to B.Th.U. per lb. it is necessary to multiply by 966.

More commonly the calorific value of a fuel is given as so many calories per gram or so many B.Th.U. per pound. Thus, if the calorific value of a coal is stated as 8,000 calories per gram, 1 gram of this coal, in completely burning, gives out 8,000 calories. The calorific value of such a coal in B.Th.U. per pound is $8{,}000 \times \frac{9}{5}$, or 14,400.

One pound of such coal, in burning, gives out sufficient heat to raise 14,400 lbs. of water through 1° F. (or, more correctly, from 39° to 40° F.). Its evaporative value is

$$\frac{14{,}400}{966} = 14{\cdot}91 \text{ lbs.}$$

The calorific value of a coal is determined by means of a special form of calorimeter (see p. 250).

Calorific Values of Fuels.

(Approximate Values)

Wood (dry)	4,500–5,100	calories	per gram.
Peat (containing 25 per cent. moisture)	3,700	,,	,,
Peat (dry)	5,000	,,	,,
Lignite (dry)	5,000–7,600	,,	,,
Coals	7,000–9,000	,,	,,
Kerosene (paraffin oil) ..	10,000–11,000	,,	,,
Petrols	10,000–11,500	,,	,,

CHAPTER V

Transference of Heat.

THERE are three methods in which heat may be transferred from one body to another—**Conduction, Convection,** and **Radiation.**

Conduction.—In this process the heat is handed on from one particle to the next, which in turn passes on the heat to the next, and so forth. If one end of a poker be placed in a fire, the other end gradually becomes warm. The heat has been transferred along the poker by conduction. The particles or molecules of which the poker is composed have *not* moved through or along the poker, but the hotter molecules have vibrated, set their neighbours vibrating, which in turn have set further neighbouring molecules vibrating. Heat is supposed to consist in the vibration of the molecules of which a body is composed; and this "sympathetic" vibration, as it were, is responsible for the transference of heat by conduction.

Some substances are better conductors of heat than others. Most metals are good conductors. Minerals, on the other hand, are, as a rule, poor conductors, and so are such substances as ebonite, bone, paper, and the like. Coal is a poor conductor of heat.

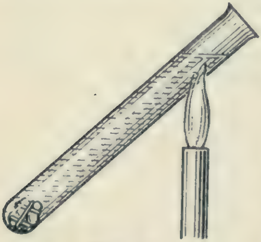


FIG. 44.

Liquids, too, except mercury, are poor conductors of heat. It is important to notice that in testing the conductivity of a liquid the heat must be supplied at the top of the liquid in order to eliminate the effects of "convection currents" in the liquid. That water is a particularly bad conductor of heat can be shown by placing a small piece of ice (wrapped in gauze to sink the ice) in a test-tube full of water (Fig. 44). The water at the top of the tube may then be boiled while the ice at the bottom remains practically unaffected, showing that little heat can have been conducted through the water to the ice.

Gases, also, are poor conductors of heat.

Convection.—When heat is transferred by convection portions of the fluid (it is always a liquid or a gas) travel through the mass of the fluid and set up "convection currents." (These are *not* electric currents.) Such convection currents are caused by changes in density of various portions of the fluid due to heating. The heated portions expand, become lighter bulk for bulk (in other words, become less dense), and tend to rise, their original place being taken by the colder, denser portions. But these colder portions in turn become heated, expand, and rise; and in this manner convection currents are set up. It is because of these currents that it is possible to heat buildings by means of hot-water pipes. The boiler in the basement heats the water on the lowest level, which water immediately rises, causes currents, and the heat is thus conveyed throughout the whole pipe-system.

Convection currents in air are similar. The following experiment is interesting. Two holes are cut in the lid of a cardboard box, also chimneys fitted over them and one of the sides is replaced by a piece of glass (Fig. 45). A lighted candle is placed inside under one of the holes, and a piece of smouldering paper is held near the other. The fumes from the smouldering paper are seen to travel down the chimney into the box and then up the other chimney under which the candle is burning, thus showing the direction of the air-current. The explanation is as in the case of liquids. The air near the burning candle becomes hot, expands, becomes less dense, rises, and colder air sweeps in to take its place.

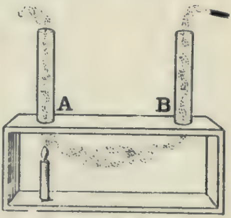


Fig. 45.

Furnace ventilation of mines is on exactly the same lines, the furnace shaft being always the upcast. Land and sea breezes may also be considered here. The specific heat of water is high. The sun's heat during the day therefore raises the land temperature more than it does the sea temperature. The air over the land is consequently heated more than that over the sea, and when the land air rises, being less dense, the cool sea breeze comes in to take its place. During the day there is therefore usually a breeze from the sea. At night-time, however, the land cools down more quickly than does the sea, and the land air tends to become cooler than the sea air. In consequence the breeze at night is often from the land to the sea.

It should be noted before leaving the subject of convection that heat is really in all cases of convection passed from one body to another by conduction. That the particles themselves move does not alter the fact that when they convey their heat to their neighbours they are for that instant in contact, and therefore hand on or conduct the heat. It is convenient, however, to distinguish the method by which heat is conveyed in a fluid from the method by which it is conveyed in a solid. Hence the use of the term "convection."

Radiation.—Heat can pass from one body to another through a vacuum. This cannot be by conduction or convection, because both of these methods require matter to convey the heat. It is now known that this heat travels by means of waves in the ether. (Ether is not matter in the ordinary sense of the word, but it is a plastic medium which is supposed to permeate all space. Matter is possibly ether under stress. The ethers of chemistry must not be confused with the above ether; they are different substances altogether.) The space above 100 miles from the earth is practically certain to be what is called a vacuum—and yet the sun's heat travels to the earth through some ninety millions of miles of such space. This heat travels by radiation, by waves in the ether.

The body which is being heated by radiation absorbs the waves which come to it. If the body allows the waves to pass through, it will not be heated.

Absorbent bodies (*i.e.*, those which are heated by radiation) are called "athermanous," while the others are called "diathermanous."

Dull, black surfaces are athermanous. Air is diathermanous, radiant heat passing through air without perceptibly warming it. Two thermometers, one with a clean bulb, the other with a coating of soot (say) on its bulb, will not register the same temperatures on being exposed to a source of radiant heat (such as a fire, one yard distant); the blackened bulb will absorb the radiation more readily and show the higher temperature.

Those substances with surfaces which readily absorb radiation also part with or radiate their heat readily. Black clothes are said to be warmer than light-coloured clothes, and this is true, provided that the temperature of the surroundings is fairly high. If, however, the temperature of the surroundings is considerably less than that of the human body, heat will be radiated from the body more easily with black clothes than with light ones. It is probable, therefore, that light-coloured material is best both for summer and winter wear, but considerations of *apparent* cleanliness and of economy, particularly in a coal-mining district, have no small influence in this matter. Roofs of houses are often whitewashed in the summer in order that they may reflect the heat instead of absorbing it. Steam-pipes are often covered with a non-conducting mixture to reduce losses due to conduction, and are then finally whitewashed to reduce losses due to radiation.

The transference of heat by radiation is usually not so easily grasped by the student as are conduction and convection. Experiments have proved that all hot bodies send out radiation—*i.e.*, rays of heat which, like rays of light, may be reflected, refracted, absorbed, or concentrated. A lens used in the sunshine as a burning-glass concentrates the radiation on to a certain point. If at this point a purely diathermanous body be placed, such a body will not be heated. If, however, the body be athermanous the heating may be sufficient to cause it to ignite; and in either case the lens will scarcely be heated at all, showing glass to be diathermanous to the sun's rays.

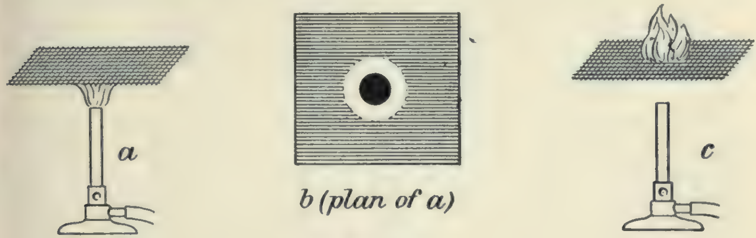
Finally, it is thought that all bodies emit radiation, and at the same time absorb radiation from other bodies. The eye is sensitive only to certain rays, and vision is possible only with such rays, but were the range wider all bodies would appear to emit light—*i.e.*, they would shine.

The Principle of the Miner's Safety Lamp.—This lamp was, in its first form, invented by Sir Humphry Davy, in 1815, though several other similar inventions were more or less contemporaneous. Colliery explosions were becoming more and more numerous, due to the opening out of the coal industry, and a deputation was sent to Davy to request him to investigate the matter and, if possible, suggest a remedy. The outcome of his labours was the well-known Davy lamp. It requires only a moment's thought to form some idea of the enormous benefits which this invention has brought to mankind in general and to miners in particular.

The action of the lamp depends upon the good conductivity of copper or iron. A metal in the form of wire gauze has a large surface exposed, and, moreover, every part of the metal is in excellent connection with every other part. If a Bunsen burner be lit, and a piece of iron gauze be depressed on to the top of the burner, the flame will not pass through the gauze until the latter has become red hot. This behaviour is due to the fact that the heat from the flame is quickly carried away by the metal gauze and distributed throughout the gauze; and the flame cannot travel through the more or less cool apertures of the gauze. For the same reasons, if a Bunsen burner be turned on and a piece of gauze be held an inch or two above the burner, the gas may be ignited *above the gauze* and will continue to burn there, but not below (Fig. 46).

In the earliest types of lamp the flame was simply surrounded by a copper gauze, and no lamp-glass was thought of. See Fig. 47 (1).

It was soon found, however, that in a current of air the flame might be blown on to one particular part of the gauze for a considerable time and eventually heat it, until, finally, the flame penetrated through the gauze. A loose cylindrical glass, some 3 inches high, was therefore placed on the outside of the gauze. (Davy had foreseen the above disadvantage, and cautioned those interested against placing the lamp in such a current of air.) The illuminating power was still very poor, and, to improve this, that part of the gauze around which the glass had been placed was taken away and a sound joint was made on the top and bottom of the lamp-glass, on the bottom to the oil-vessel, on the top to the gauze, as in



b (plan of a)

Fig. 46.

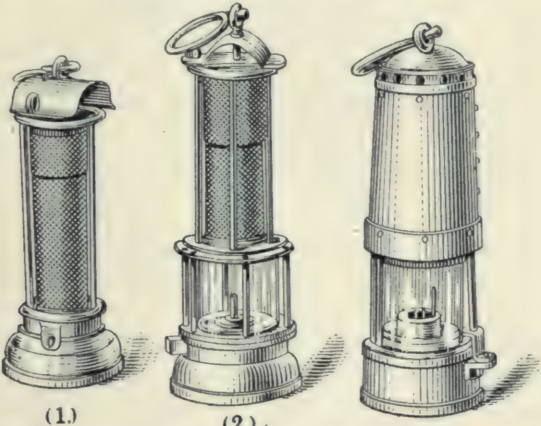

(1.) (2.) (3.)

Fig. 47.—Miners' Lamps.

Fig. 47 (2). A shield was then provided for the gauze, as in Fig. 47 (3). Most of the present-day lamps are of this pattern with certain refinements, as in the Mueseler type, where a chimney is introduced; or in the method of lighting the lamp by means of platinum wire, as in the Protector type; or in the method of locking the lamp; or in having special conduits for the air supply from above which, among other advantages, enables a test for inflammable gas to be carried out near the roof and in roof cavities. The reason that the lamp is safe in explosive mixtures of air and imflammable gas should be clear, but it is well to understand exactly what happens. If the lamp is placed in an *explosive* mixture, the whole of the "gas" inside the lamp takes fire, but, due to the good conductivity of the metal gauze, the flame does not pass through it, and the temperature reached by the gauze is below the ignition point of the explosive mixture. The burning of such "gas" disturbs the air currents in the lamp and allows insufficient air to come to feed the lamp-flame, so that the lamp is often automatically extinguished.

If, on the other hand, the atmosphere contains a certain amount of inflammable gas—less than that required to form an explosive mixture—*i.e.*, less than 5·6 per cent. methane—the lamp-flame tends to become larger due to the combustion of the inflammable gas near the source of heat. On lowering the flame till there is hardly a glimmer, the inflammable gas may be seen burning in the form of a pale blue cone on the top of the small and practically non-luminous testing flame. According to the height of the cap, the amount of firedamp present may be roughly estimated. The heights of cap and the corresponding percentages of methane are given on p. 185.

Note on the Gauze.—Davy found that the best gauze was copper gauze, with twenty-eight apertures to the linear inch, the diameter of the copper wire being $\frac{1}{40}$ inch. This yields 784 apertures to the square inch.

Iron gauze, however, is now used in general owing to the fact that copper gauze is rather easily burned through by a hot lamp-flame. Moreover, it is now customary to use two or three gauzes instead of one.

The Mechanical Equivalent of Heat.

Work.—If a body weighing 10 lbs. is *raised* 4 feet then the work done is 40 foot-pounds. Similarly, if a body weighing 4 lbs. is *raised* 7 feet the work done is 28 foot-pounds. The weight of a body, of course, acts vertically downwards, and when a body is raised it is moved directly against its weight, or in other words, " a certain resistance is overcome through a certain space." The amount of work done is, we have seen, equal to the product of this resistance by the space through which it is overcome. The unit of work is the foot-pound, and it represents the work done when a body weighing 1 lb. is raised 1 foot, or when a force of 1 lb. moves its point of application by 1 foot. The time taken in the operation is of no account, as far as the work done is concerned.

The *rate* of doing work is called **power.** The unit of power is the **Horse Power** (h.p.), and it is defined as a rate of work of 33,000 foot-pounds *per minute.*

Watt first used this figure as a means of comparing the power of his steam engines with the power of a horse. He found from experiments that, on an average, a horse does about 22,000 foot-pounds of work per minute, and, in order to leave a generous margin for the purchasers of his engines, he took one and a half times the above figure as his standard.

If a body weighing 40 lbs. be raised 30 feet in 1 minute, then the rate of doing work (or the power of the machine performing the above) is 1,200 foot-pounds per minute,

or $$\frac{1200}{33000} = \frac{1}{27 \cdot 5} \text{ h.p.}$$

Note.—33,000 foot-pounds per minute $= \frac{33000}{60}$ foot-pounds per second $=550$ foot-pounds per second.

1 h.p. is therefore also equal to 550 foot-pounds per second.

E.g., calculate the h.p. expended when 3·3 tons of coal is raised in a shaft through a distance of 500 yards in 30 seconds.

Work done in 30 seconds $= 3 \cdot 3 \times 2240 \times 500 \times 3$ foot-pounds.
Work done per minute $= 3 \cdot 3 \times 2240 \times 500 \times 3 \times 2$ foot-pounds.

$$\text{H.p.} = \frac{3 \cdot 3 \times 2240 \times 500 \times 3 \times 2}{33000} = 672 \text{ h.p.}$$

Energy is defined as the capacity for doing work. A body weighing 6 lbs. after being raised 5 feet possesses "potential energy" of 30 foot-pounds, as *that* is the amount of work the body is capable of doing if it is allowed to fall from its position.

A flying rifle-bullet possesses **Kinetic Energy**—*i.e.*, energy due to its motion. It is capable at any moment of doing some work. This kinetic energy, of course, is gradually transformed as the velocity of the bullet decreases.

Energy, like mass, cannot be destroyed, but merely passes from one form to another. This is a fundamental principle, proved by many experiments.

In the above cases of the falling body and the flying rifle-bullet the potential energy and the kinetic energy appear as heat energy. When the body falls, or when the bullet is on its flight, heat is formed. In the sudden transformation of mechanical energy into heat energy, as in the case of a pick striking a hard stone, the heat is often apparent, sparks being emitted.

A reverse process takes place in the steam engine. Heat, in this case, is supplied to the water to convert it to steam, which then acts on the piston, moves it, and so performs work.

Now is there any definite relation between the total amount of work done and the total amount of heat developed? **Dr. Joule** of Manchester carried out a number of careful experiments and discovered that there was a very definite relation, and this relation is called the **mechanical equivalent of heat.**

Joule determined that 1 lb. of water was increased in temperature by 1° F. by the work done upon it during the descent of 778 lbs. through 1 foot.

In other words, **1 British Thermal Unit = 778 foot-pounds** work.

Similarly, 1 calorie = 3·08 foot-pounds work; 1 C.H.U.

(Centigrade Heat Unit or 1 water-pound) $= 778 \times \frac{9}{5} = 1400$ foot-pounds work.

The principle of the method employed by Joule may be seen from the diagram (Fig. 48). The weights *W* in falling rotated the spindle *C* and paddles, which churned up the water, so doing work on it. The water was prevented from rotating by introducing fixed partitions, as shown in section below. The work done was obtained by multiplying the weights *W* by the distance they fell, and the heat developed was measured by multiplying the rise in temperature of the water by (the mass of the water + the water equivalent* of the apparatus). The handle was so arranged that the weights could be raised without moving the paddles, and several refinements were made to eliminate friction.

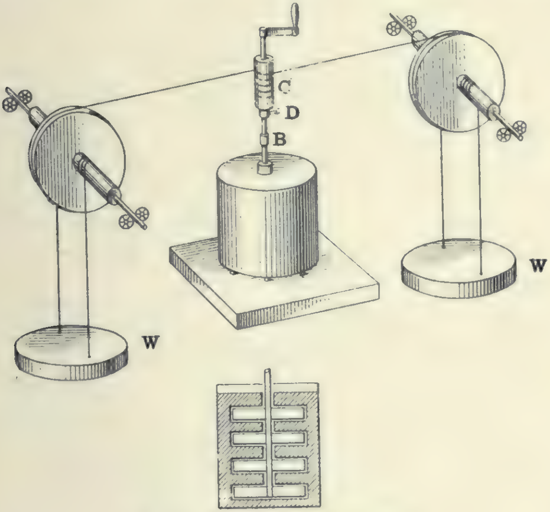


FIG. 48.—JOULE'S APPARATUS.

The **erg** is the scientific unit of work. It represents the work done when a body weighing **1 gram is raised 1 cm.**

It can be shown that 1 calorie = 42 million ergs. The above

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* See page 250.

values for the mechanical equivalent of heat have been verified by other experimenters working in some cases on quite different lines.

It is useful now to compare the amounts of mechanical energy theoretically obtainable from various fuels whose calorific values are known.

SUBSTANCE.	ENERGY IN 1 LB.		
	C.H.U. CALORIES.	B.TH.U.	FOOT-POUNDS.
Wood (dry)	4,800	8,640	6,720,000
Peat (25 per cent. moisture)	3,500	6,300	4,900,000
Peat (dried)	5,000	9,000	7,000,000
Lignite (dried)	6,500	11,700	9,100,000
Coal (good)	8,500	15,300	11,900,000
Kerosene (paraffin oil) ..	11,000	19,800	15,400,000
Petrols	11,000	19,800	15,400,000

Examples.—1. An oil engine uses 0·65 lb. kerosene per h.p. per hour. What is the over-all efficiency of the engine ?

$$
\begin{aligned}
0{\cdot}65 \text{ lb. kerosene} &= 19800 \times 0{\cdot}65 \text{ B.Th.U.}\\
&= 15400000 \times 0{\cdot}65 \text{ foot-pounds.}\\
1 \text{ h.p. for } 1 \text{ hour} &= 33000 \times 60 \text{ foot-pounds.}\\
\therefore \text{Per cent. efficiency} &= \frac{33000 \times 60 \times 100}{15400000 \times 0{\cdot}65}\\
&= 19{\cdot}8 \text{ per cent.}
\end{aligned}
$$

2. 1,600 lbs. of coal are required per hour to develop 700 h.p. What percentage of the available energy is being employed usefully ?

$$
\begin{aligned}
1600 \text{ lbs. coal} &= 1600 \times 11900000 \text{ foot-pounds work.}\\
700 \text{ h.p.} &= 700 \times 33000 \text{ foot-pounds per minute}\\
&= 700 \times 33000 \times 60 \text{ foot-pounds per hour.}
\end{aligned}
$$

$\therefore$ Percentage usefully employed

$$
= \frac{700 \times 33000 \times 60}{1600 \times 11900000} \times 100 = \mathbf{7{\cdot}28 \text{ per cent.}}
$$

CHAPTER VI

HYGROMETRY—MOISTURE IN THE AIR.

Evaporation.—Liquids tend to evaporate under normal atmospheric pressures at temperatures well below their boiling-points. There is always some water vapour in the atmosphere because of the continual evaporation of water from the seas, lakes, and rivers, but the quantity present is very variable. It is important for the mining student to be familiar with the estimation of the moisture in the air, as the humidity or wetness of the mine air influences the health of the persons employed in the mine, may indicate the outbreak of an underground fire, and may prevent or assist an explosion.

Vapour Pressure of Liquids.—The rate of evaporation of a liquid is increased by (1) rise in temperature; (2) decrease in pressure; (3) decrease in the quantity of the vapour in the atmosphere into which the liquid is evaporating. This last condition holds where there is a current of air passing over the liquid, and in such cases the rate of evaporation is greater than where the air is practically at rest. The molecules of water may be imagined as leaping from the surface of the water, the majority returning back to the liquid, but some leaping so far as to be carried away by the air, and so contributing their share to the water vapour in the atmosphere. Warming the water causes the molecules to leap from the surface in greater number and with greater velocity, and consequently accelerates evaporation. Increasing the pressure of the air, however, prevents the molecules from leaping so far, and reduces the rate of evaporation.

The air, however, cannot hold more than a certain quantity of water vapour at any particular temperature, and when the atmosphere is carrying its maximum quantity of water vapour (which maximum quantity rapidly increases with rise in temperature) the air is said to be saturated with moisture.

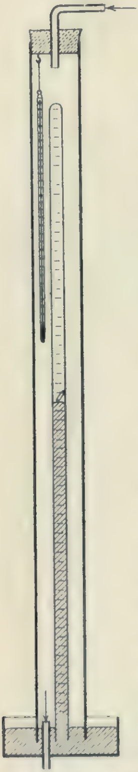

Fig. 49.

The laws governing the pressures exerted by vapours are known as **Dalton's Laws.** They state:

1. The pressure which a *saturated* vapour exerts depends only on the temperature.

2. The pressure which a mixture of gases and vapours exerts is the sum of the pressures which each would separately exert if it alone occupied the space filled by the mixture.

The first law may be verified by the following experiment:

Take a barometer, such as that described on p. 30, and mark the height of the mercury. Now introduce by means of a pipette about 1 c.c. (one cubic centimetre) of water under the barometer tube in the basin. The water rises to the top of the barometer into what was the Torricellian vacuum and depresses the mercury by a certain amount—which is governed entirely by the temperature. If the barometer tube be now surrounded with a glass jacket through which warm water or steam is slowly circulated, the increase in temperature of the water in the barometer tube causes the mercury to be depressed further (see Fig. 49). If the temperature be raised still more, the depression of the mercury continues, until the surface of the mercury in the tube is level with the surface of the mercury in the basin. And this occurs when the boiling-point of water is reached. By similar experiments to the above Regnault found the pressure of saturated aqueous vapour at different temperatures and expressed it in millimetres of mercury gauge. This pressure is also called the Tension of Aqueous Vapour. Values are given in the following table. They are employed in calculating the humidity of the atmosphere when using Dew-Point Hygrometers.

PRESSURE OF AQUEOUS VAPOUR IN MILLIMETRES OF MERCURY.

t° C.	*Mm.*	*t° C.*	*Mm.*	*t° C.*	*Mm.*
−10	2·08	0	4·60	10	9·17
− 9	2·26	1	4·94	11	9·79
− 8	2·46	2	5·30	12	10·46
− 7	2·67	3	5·69	13	11·16
− 6	2·89	4	6·10	14	11·91
− 5	3·13	5	6·53	15	12·70
− 4	3·39	6	7·00	16	13·54
− 3	3·66	7	7·49	20	17·39
− 2	3·96	8	8·02	50	91·98
− 1	4·27	9	8·57	100	760·00

When, however, the vapour is present in insufficient amount to cause saturation it exerts a pressure which is directly proportional to its mass in a given volume—or, in other words, to its density. This is really only another statement of Boyle's Law (p. 52). Boyle's Law states that for a given mass of gas the pressure varies inversely as its volume. Now the volume of a given mass of gas varies inversely as its density $\left(D = \frac{M}{V}\right)$. It follows therefore that the pressure of a gas varies directly as the density, and the same law holds approximately for unsaturated vapours. **A gas may be regarded as a vapour well removed from its liquid state by conditions of temperature or of pressure or of both.**

Quantity of Water Vapour in One Cubic Foot of Saturated Atmosphere.—The mass of water vapour necessary to saturate 1 cubic foot of air at different temperatures is given in the following table:

Temperature in °F. ..	40°	50°	60°	65°	70°	75°	80°	85°
Grains of water vapour per cubic foot ..	2·9	4·1	5·9	6·8	8·0	9·4	11·0	12·6

Dew Point.—Warm air can hold more moisture per cubic foot than can cold air. When, therefore, warm air containing moisture, but not saturated, is cooled down a temperature is reached at which the now cooler air is saturated and begins to deposit its moisture in the form of dew. This temperature is called the Dew Point.

The **Relative Humidity** of the air is the ratio of the amount of water vapour present to the maximum amount required for saturation at the same temperature. It may be expressed as a percentage. Thus, if there is 1 gram of water vapour in a certain volume of air, and 5 grams of water vapour is the total amount necessary to saturate an equal volume of air at the same temperature, the relative humidity is $\frac{1}{5}$ or $\frac{20}{100}$, or 20 per cent. This is also called the **Percentage Saturation.**

The methods of measuring the amount of water vapour in the air are divided into Chemical Methods and Physical Methods, and the apparatus used in each case is called an hygrometer.

Chemical Hygrometer.—This is the most direct and most accurate method of measuring the amount of water vapour in a certain volume of air.

The apparatus consists of two U-tubes containing dry calcium chloride connected to a large vessel full of water (Fig. 50). The volume of the vessel is known, or can be found by allowing the outflowing water to run into a measuring jar. The U-tubes containing the calcium chloride are first accurately weighed and then connected up, as shown, to the large vessel, often called an aspirator. Water is run out from the tap at the bottom, and the air is by this means drawn through the tubes, where it yields up its moisture to the hygroscopic calcium chloride. When the aspirator is empty, the U-tubes may be temporarily removed, the aspirator again filled with water, the tubes reconnected, and a second volume of air drawn through, as before. The process is repeated until an appreciable increase in weight of the U-tubes and calcium chloride is obtained. This increase is the weight of the water vapour in the volume of air which has been drawn through the tubes.

The percentage saturation or relative humidity may be found by reference to tables, or by a second experiment in which an equal volume of air to the above is first bubbled through water at the temperature of the air and then drawn through the calcium chloride tubes. The increase in weight now gives the weight of water vapour in the volume of saturated air, and this weight divided into the weight of water vapour obtained in the first experiment gives the relative humidity. The result must be multiplied by 100 if desired as a percentage.

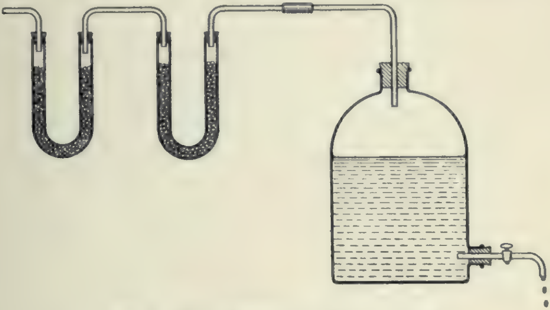

FIG. 50.—CHEMICAL HYGROMETER.

Physical Hygrometers.—If a little air—*not* separated from the rest of the atmosphere—be cooled down, the pressure of its water vapour will be precisely the same as the pressure of the water vapour in the surrounding atmosphere. Now from Regnault's tables we know the pressure of aqueous vapour at saturation—or, in other words, the pressure of water vapour at the dew point. If, therefore, by some means the air be cooled down until it begins to deposit dew, and this temperature be noted, the pressure of the water vapour in the air may be found immediately by reference to the table on p. 77. Also, it is an easy matter to take the temperature of the uncooled air, and by reference to the same table find out the saturation pressure at this latter temperature.

Now, the relative humidity is defined as the ratio

$$\frac{\text{mass of water vapour present}}{\text{mass of water vapour required for saturation at the same temperature}},$$

and from the consideration of Boyle's Law (p. 77) this ratio may be written—

$$\frac{\text{pressure of water vapour present}}{\text{pressure of water vapour if saturated at the same temperature}}.$$

The **Relative Humidity** may therefore be easily calculated from the above two readings of the table.

E.g., the temperature of the air is 15° C., and the dew point is found to be 5° C. What is the relative humidity ?

Saturation vapour pressure at 5° C. = 6·53 mm.
,, ,, ,, ,, 15° C. = 12·70 ,,

$$\therefore \text{ Relative humidity} = \frac{6{\cdot}53}{12{\cdot}7} \text{ or } \left(\frac{6{\cdot}53 \times 100}{12{\cdot}7}\right) \text{ per cent.}$$
$$= \mathbf{51{\cdot}4 \text{ per cent.}}$$

Some hygrometers, such as the Daniell's and the Dines', are therefore merely instruments for finding the dew point.

Daniell's Hygrometer.—This instrument consists of two glass bulbs communicating with each other through a glass tube (Fig. 51). The air has been removed from the apparatus, and some ether (a very volatile liquid boiling at 35° C. under normal pressure) enclosed before sealing up.

Bulb *A* has on it a silvered or blackened ring in order that the formation of the dew may be more easily perceived, and a thermometer is in communication with the ether in this bulb. A second thermometer fixed to the stand gives the temperature of the outside air. The other bulb of the hygrometer is covered with a muslin rag.

To find the dew point, the ether is transferred to bulb *A* by tilting the instrument, and some more ether is poured on to the muslin cloth. This latter ether quickly evaporates into the air, and in doing so cools down the bulb inside the muslin.

The cooling down condenses the ether vapour inside, causes the ether in bulb *A* to evaporate and distil over, and so lowers the temperature of *A*. The process continues, more ether being poured on to the muslin if necessary, until the temperature is reduced to the dew point, and a film of dew gathers on the silvered ring. This temperature is noted on the thermometer in bulb *A*. The apparatus is now allowed to warm up, and the temperature at which the dew disappears is read on the same thermometer. The mean of these two readings is taken as the Dew Point. The Relative Humidity is found from the tables as in the example on p. 80, the temperature of the air being obtained from the thermometer attached to the stand.

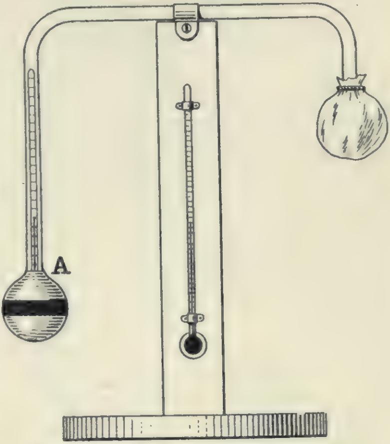

FIG. 51.—DANIELL'S HYGROMETER.

Daniell's hygrometer gives results which are only approximate.

Dines' Hygrometer.—This apparatus for finding the dew point is much more sensitive and reliable than the Daniell's. A section is shown in Fig. 52.

Cold water, containing some ice if necessary, is run from the tank *A* through the tube to the chamber *B*, which has a blackened or silvered surface, and

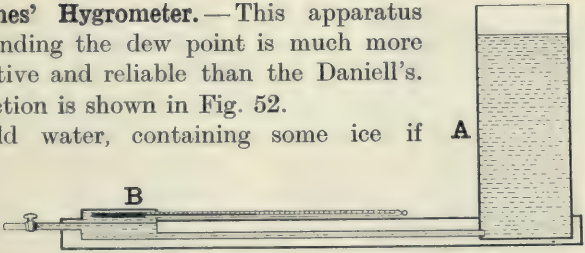

FIG. 52.—DINES' HYGROMETER.

immediately below this surface is the bulb of a sensitive thermometer.

To determine the dew point, the cold water is allowed to flow through the apparatus until a film of dew forms on the silvered surface, at which point the thermometer is read. The flow of cold water is now cut off and somewhat warmer water added to the tank. The warmer water is then run through the tube to the chamber *B* until the dew disappears, when the temperature is also noted. The mean of the observed temperatures is taken as the dew point.

Calculate the Relative Humidity as in the example on p. 80, the air temperature being obtained from another thermometer.

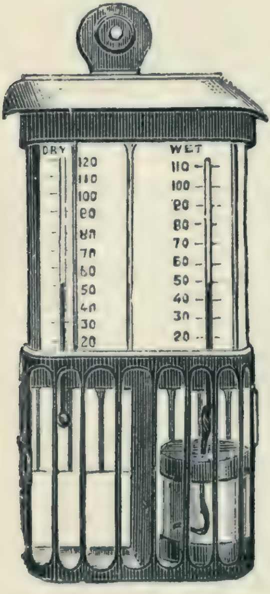

Fig. 53.—Wet- and Dry-Bulb Hygrometer.

Wet- and Dry-Bulb Hygrometer.—This is the type used at most mines, and consists essentially of two thermometers placed side by side. Round the bulb of one of them is wrapped some muslin which leads to a vessel containing water, so that the muslin and the bulb round which the muslin is wrapped are always wet. The water held in the muslin is continually evaporating and cools down the thermometer bulb with which it is in contact, so that this wet-bulb thermometer normally reads lower than the dry-bulb thermometer. Moreover, the amount of cooling down which is produced depends upon the rate of evaporation, which in turn is governed by the amount of moisture in the air—the rate of evaporation being greatest when the moisture in the air is least, and *vice versa*. Clearly, if the two thermometers have the same reading there is no evaporation taking place, and the air is saturated.

The Relative Humidity is found from the readings of the wet- and dry-bulb thermometers by reference to tables which have been drawn up by Glaisher (see Appendix).

Example.—Dry-bulb thermometer = 60·0° F.
Wet- „ „ = 54·4° F.
Difference = 5·6° F.

Then from the tables the relative humidity = 68 per cent.

Knowing the weight of water vapour necessary to saturate 1 cubic foot of air at this temperature, it is easy to calculate the weight of water vapour present in 1 cubic foot of air whose saturation is 68 per cent.

Applications.—Hygrometers, according to the Coal Mines Act, 1911, must be read in the mine daily in the main intake airways near the bottom of the downcast shaft, and weekly in the main return airways. A record must be kept of the readings.

Health of the Workmen.—The human body is continuously giving off moisture, organic acids, etc., in the form of perspiration; and partly by this means the body temperature is prevented from rising. When the temperature of the surrounding atmosphere is raised, the rate of perspiration tends to increase in order to assist still further in keeping the body cool. If this perspiration is to be easily disposed of by the body the air must not be too heavily laden with moisture, and must be passing along fairly rapidly. In deep mines the temperature is high, sometimes up to 100° F. If the mine air at, say, 85° F. is practically saturated with moisture, the conditions are serious. Working in such an atmosphere the body becomes uncomfortably hot—even to a dangerous degree—and efficient work is impossible.

However, work in a current of fairly dry air at a temperature of 90° F. will result in no undue amount of such discomfort, and 100° F. under these conditions will generally have no serious effects on the health.

Further, Dr. Haldane has shown that when the temperature of the air is above 70° F., the wet-bulb temperature is of itself of great hygienic importance. The evaporation of moisture from the wet bulb may be likened to the evaporation of perspiration from the body, and if such evaporation be not proceeding quickly enough to maintain the temperature below a certain point, harmful results ensue. The maximum safe wet-bulb temperature is about 80° F. under normal working conditions.

Explosions.—On the other hand, excess of moisture retards and may prevent a coal-dust explosion, though the presence of a trace of moisture is found rather to have the opposite effect. The air in a mine is never perfectly dry. A mine is commonly spoken of as a dry mine where there is little or no water coming from the strata into the mine.

In general, therefore, the drier the mine air the more danger of an explosion. In a mine naturally wet throughout there is no likelihood of forming a " cloud " of coal-dust and, in consequence, little danger of an explosion of coal-dust. Mine dust containing 30 per cent. of moisture is generally incapable of propagating an explosion. Indeed, taking the average ash of a mine dust as 40 per cent., 20 per cent. of moisture would probably be sufficient to prevent propagation of the explosion in the majority of cases.

Underground Fires.—One of the commonest indications of a gob-fire is the " sweating " of the strata. This " sweating " is merely the result of the condensation of water vapour and other vapours (derived from the heating of the coal) on the sides, roof, and floor of the roadways. The relative humidity of the return air in such cases and its temperature are often considerably increased; and these increases are indicated by the hygrometer readings (which are taken daily) before the " sweating " of the strata to any marked extent is noticeable. The manager is consequently enabled to take the matter in hand at once.

LIGHT AND PHOTOMETRY.

Light is that which enables the eye to see—in other words, "light is the physical cause of the sensation of sight." If a Bunsen burner be lit in a darkened room, the flame is scarcely visible, but, if a piece of platinum be held in the flame, the platinum is rapidly heated to a white heat and emits light. The flame of the Bunsen burner of itself emits radiant heat, which radiation may easily be felt by the hand placed a short distance away from (*not* above) the flame. When the platinum is introduced, the radiation still takes place, but some of it takes on the nature of light, the platinum becoming luminous. Light has been seen to be closely allied to radiant heat. Light travels by means of waves in the ether, just as does radiant heat. Like radiant heat, also, light travels in straight lines, for the vibrations of the ether are of minute dimensions, and for the purposes of Geometrical Optics rays of light (in the same medium) are always regarded as travelling in straight lines. Light travels with the enormous velocity of 186,000 miles per second.

Candle Power.—To compare the lighting or illuminating powers of various lamps or sources of light, a standard has been fixed. A candle-power is defined as the illuminating power of a sperm candle weighing one-sixth of a pound and burning at the rate of 120 grams per hour. This is a crude standard, so a standard pentane flame is often employed. Pentane is a hydrocarbon of the paraffin series (see p. 190).

Photometry.—If a source of light 1 inch away from a screen illuminates a portion of the screen to the same extent as does a second source of light placed 2 inches away, it is clear that the latter source of light has the greater illuminating power. If a candle be employed to illuminate a book sufficiently to enable one to read, it is necessary to have the candle flame fairly near. If, however, an ordinary electric light be employed (of some 16 candle-power, say), the light may be placed at some considerable distance away without causing inconvenience. As rays of light leave their source they become spread about. Referring to Fig. 1, p. 3, the rays of light impinging on plate *C* are so much farther apart than they are on plate *B* that *C* has to be made four times the area of *B*, and the intensity of illumination of *C* is only one-quarter that of *B*. In general, the intensity of illumination is inversely proportional to the square of the distance from the source of light. In the case, therefore, of equal illumination being obtained on a screen from two sources of light, X and Y, X being distant 2 inches from the screen and Y being distant 3 inches from the screen:

$$\frac{\text{illuminating power of X}}{\text{illuminating power of Y}} = \frac{2^2}{3^2}$$
$$= \frac{4}{9}$$

or, if X is 4 candle-power, Y is 9 candle-power.

Photometers are apparatus for comparing the lighting powers of various lamps, etc., by adjusting the distances of the lights from the screen until equal illumination is obtained on the screen from each light. The ratio of the lighting powers is calculated from considerations of the "law of inverse squares," as above.

Rumford's Photometer.—In this type a short piece of wood—an ordinary lead pencil is convenient—is stood vertically on the table about 2 inches in front of a piece of white unglazed paper supported vertically to form a screen. A standard candle is lit and placed so that a good shadow is cast on the screen by the lead pencil. The lamp whose candle-power

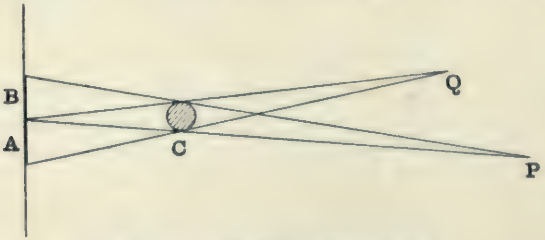

Fig. 54.—Rumford Photometer.

is required is now moved about until a second shadow is obtained in contact with the former shadow and of equal intensity.

Fig. 54 shows the arrangement, P and Q representing the sources of light, and B and A their respective shadows. The distances of the candle and of the lamp from the screen are measured. Let the candle be 20 inches and the lamp 14 inches from the screen. Then the illuminating power of the lamp is $\frac{14^2}{20^2}=\frac{7^2}{10^2}=0{\cdot}49$ candle-power, or just less than half a candle-power.

Bunsen's Photometer.—This apparatus may be easily made as follows:

Make a grease spot on a piece of clean white paper by means of a drop of molten paraffin wax. Scrape off the surplus wax when cold. This spot allows more light to pass through than does the rest of the paper, as may be seen by holding up the paper in front of a source of light, when the grease spot will appear brighter than the rest of the paper. Mount this piece of paper on a wire frame with the grease spot in the middle and support the frame on a stand. Arrange the stand on a length of wood—some 3 yards long and graduated in half inches.

If, now, a lighted candle be stood vertically on the wooden scale, and the grease spot be viewed from the far side, the spot will be brighter than the rest of the paper. But if a similar lighted candle be placed on the scale at exactly the same distance from the paper as the former but on the opposite side, then, since the illumination on both sides is equal, the spot will be practically indistinguishable from the rest of the paper.

Fig. 55 shows diagrammatically the arrangement of the grease-spot photometer for comparing the candle-powers of electric lamps. A room with dull black walls with all light excluded is necessary for accurate work and a box is often employed, as shown, to shut off all light except that proceeding from the lamps being tested. M and M_1 are mirrors arranged so that both sides of the paper-screen may be seen together and accurate comparisons made.

To find the candle-power of a miner's lamp, a candle (standard) is lit and placed at one end of the scale and the lamp placed at the other. The screen of paper with the grease spot is then moved either towards or away from the candle until the spot is indistinguishable from the rest of the paper. The distance from the candle to the screen is now noted. Let it be 36 units. The distance from the lamp to the screen is also noted. Let it be 30 units; then, from the "inverse square" law, the candle-power of the lamp is $\frac{30^2}{36^2} = 0{\cdot}69$

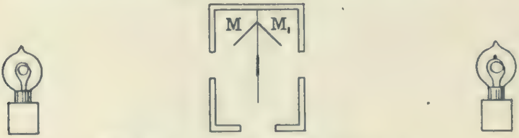

FIG. 55.—BUNSEN PHOTOMETER.

Flicker Photometer.—This is one of the more recent types of photometer and is more accurate than the others. A white disc whose edges are truncated in a special manner (Fig. 56) is rapidly rotated by clockwork between two sources of light, one of known candle-power. The axis of the disc is kept in line with the sources of light; and, while rotating, the disc is moved either away from or towards the source of light whose candle-power is desired until, on looking at the edge of the disc from above (the line of sight being deflected from the hori-

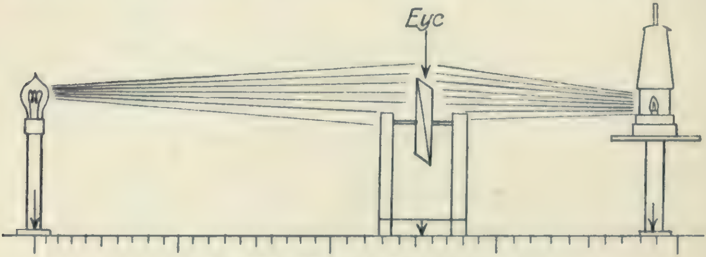

FIG. 56.—FLICKER PHOTOMETER.

zontal by means of a mirror at 45°), no flicker is observable. The intensities of the light on each side of the disc then being equal, the distances of each source of light from the disc are taken and the candle-power of the lamp or light in question found by applying the "inverse square" law.

Candle-Powers of Some Miners' Lamps.—An improved light underground results in several advantages: (1) A saving in time in most of the operations; (2) a reduction in the number of accidents; (3) a reduction in the number of cases of the eye disease nystagmus. The following figures are taken from a paper by Professor McMillan read to the Midland Branch of the National Association of Colliery Managers on June 5, 1920:

Miners' Oil Lamps.			*Miners' Electric Lamps.*		
Lamp.	*Candle-Power.*		*Lamp.*	*Candle-Power.*	
	At Start.	*After* 10 *Hours.*		*At Start*	*After* 10 *Hours.*
Oldham	2·01	not obtained	Ceag (acid)	1·09	0·83
			Ceag (acid)	1·13	0·86
Davis Kirkby	0·99	0·89	Ceag (jellac)	0·97	0·77
Davis Kirkby (improved burner)	1·03	0·84	Ceag (jellac)	0·94	0·75
			Fors (small)	0·86	0·58
Best (No. 1)	0·91	0·82	Oldham	1·07	0·99–0·9
Protector	0·63	0·61	Fuller	1·65	1·02
Best (No. 2)	1·21	not obtained	Fors (large)	1·30	1·01
			Davis Edison	1·32	1·07–0·96
Hailwood (combustion tube)	1·13	0·81	Pearson	1·15	0·74
			Kingsway	1·02	0·93–0·89
Davis Kirkby	0·83	0·77	Gray Sussman	1·61	1·11
Cremer	0·74	0·70			

The following table shows the influence on the number of cases of nystagmus of the introduction of electric lamps at one of the collieries belonging to the Butterley Colliery Company:

Period.	*Number of Underground Employees.*	*Number of Fresh Cases for the Year.*	*Per Cent. of all Cases on Full Compensation for Nystagmus.*	*Per Cent. of Fresh Cases.*
1913–14	1698	23	1·08	1·35
1914–15	1664	22	1·14	1·32
1915–16	1640	13	0·61	0·79
1916–17	1849	15	0·86	0·81
1917–18	1771	7	0·73	0·39
1918–19	1635	9	0·98	0·55
July, 1919, to Dec., 1919	1983	3	0·75	0·15

Electric lamps were introduced in July, 1915.

PART II.—CHEMISTRY

CHAPTER VII

Physical Change and Chemical Change.

Physical Change.—When water is cooled sufficiently it turns to ice; when heated sufficiently it turns to steam. In each of these cases the change is said to be a Physical Change, as the composition of the water is the same as that of the ice or of the steam. Similarly, when iron is heated strongly enough it melts, and in place of an ordinary metallic-looking solid there appears a white incandescent liquid. The change, again, is merely physical.

Chemical Change.—When coal burns in air, however, there is change of a different nature. Coal, a shiny black solid, on heating, takes fire and, after a while, it supplies of its own accord sufficient heat to enable it to continue burning until the combustion is complete. Various vapours or gases are given off in the process, and finally there is left an " ash," weighing often less than one-tenth of the weight of the original coal. The ash, of course, is only a fraction of the substances formed; the gases have escaped into the atmosphere. This is an example of chemical change—or, rather, a number of chemical changes.

A simpler example of chemical change is the rusting of iron. When iron rusts, a bright, hard, tough metal is converted into a brown, flaky (almost earthy) substance—a most decided change. Moreover, the weight of the rusted iron is greater than the weight of the original iron. Indeed, if the whole of the iron is turned to rust the weight of such rust is much greater than the weight of the iron from which it was derived. Phosphorus, burning in air, provides a third example of chemical change. Phosphorus is at ordinary temperatures a white to yellow, waxy-looking solid which will take fire of its own accord in air. When it does so, white fumes are formed which condense on any cool surfaces to a white solid. If all the white solid be collected, it is found to weigh more than the original phosphorus.

A fourth example of chemical change is seen in the smelting of iron, where an ore of iron of earthy appearance is converted into the metal. In this case the changes are complex (as in the burning of coal), but the weight of iron obtainable is much less than the weight of ore.

In a chemical change, therefore, there is a change in the composition of the substance, which change involves loss or gain in weight. This loss or gain in weight, however, is apparent only when the substances taking part in the chemical change are considered more or less individually. If *all* the substances concerned are considered, there is found to be *no loss* and *no gain* in weight. What is lost by some of the substances is gained by the others, and *vice versa*.

Conservation of Mass.—The above statement may be verified by the following experiment. (N.B.—Phosphorus must not be touched by the hand.) Take a strong glass flask of about 200 c.c. capacity and introduce a small piece—about 1 gram—of yellow phosphorus. Close the flask with a good fitting rubber stopper through which passes a piece of glass tubing fitted with a short length of rubber tubing closed by a clip (see Fig. 57). Weigh the flask, contents, and fittings. Now warm a part of the flask very gently, and then by tapping bring the phosphorus on to the warm spot. The phosphorus takes fire and white fumes, which soon condense, are seen in the flask. On cooling, again weigh the flask, contents, and fittings. There is found to be no loss or gain in weight, and therefore no change in mass.

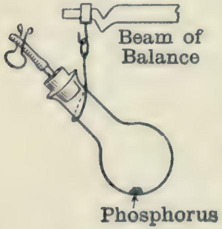

FIG. 57.

Thousands of experiments go to prove the same principle—

viz., that matter can be neither created nor destroyed, but only altered in its form. The Law of Conservation of Mass may be stated thus: **"The mass of matter which takes part in any change, whether physical or chemical, remains unaltered."** The law is analogous to that of the Conservation of Energy.

Note.—The object in closing the flask in the above experiment with a clip and tubing is to enable the student to make the following interesting additional experiment. After the flask, etc., has been weighed a second time, immerse the neck and tubing under water and open the clip. Water rushes into the flask and is found to fill about one-fifth of the volume of the flask, if the pressure inside the flask is adjusted to atmospheric by making the water levels inside and outside the flask coincide· It would appear, therefore, that about one-fifth of the air has been " used up " by the phosphorus in burning to form the white solid yielded by the fumes. The remaining " air " in the flask, if now tested, will be found to extinguish a lighted taper or candle.

Elements, Compounds, and Mixtures.—It is possible to separate from certain substances certain other simpler substances. If chalk be heated strongly it breaks up into two other substances, one a white solid known as lime, and the other a colourless gas known as carbon dioxide. And by special treatment lime can be split up into two substances—calcium (a metal), and oxygen (a colourless gas). Likewise carbon dioxide can be split up into carbon (a non-metallic solid) and oxygen (a colourless gas). Now calcium, oxygen, and carbon cannot be split up into anything simpler, and such bodies as these are called **"elements."** An element may therefore be defined as **a substance which cannot be split up into any simpler substances.**

On examining the quantities of the various elements present in chalk it is found that the calcium, oxygen, and carbon are always present in the same proportion by weight. They are always present in the proportion of 40 parts of calcium, 12 parts of carbon, and 48 parts of oxygen, giving 100 parts of chalk. Such substances as chalk are called **chemical**

compounds. A compound is defined as **a substance in which two or more elements are chemically united in certain constant proportions by weight.** A compound is usually entirely different from any of the elements of which it is composed, and its properties are *not* those which would be expected as the *average* of those of the constituent elements. The chemical name for chalk is calcium carbonate.

A **mixture,** on the other hand, consists of two or more elements or compounds, often very intimately associated but never chemically combined. The properties of a mixture *are* usually the *average* of those of the components, and a mixture may generally, by easy mechanical means, be resolved into its constituents, whereas a compound *cannot*. Moreover, compounds are formed with the accompaniment of heat changes and sometimes light, which is not the case with mixtures.

Some of the commoner elements are given on p. 95; a complete list will be found in the Appendix.

Elementary Examination of the Atmosphere.

When mercury is gently heated for some time in a limited supply of air, it is noticed that about one-fifth of the air is used up and that red particles have formed on the surface of the mercury. On testing the "air" which remains over, it is found to be quite different from the original ordinary air inasmuch as it will extinguish a burning taper and animals cannot live in it. Now, if the red particles be collected and heated strongly a gas is given off which is found to be "opposite in nature" from the above residual "air," as it will not only enable a taper to burn in it most vigorously, but will ignite a glowing splint of wood and cause it to burn brilliantly. Moreover, in a small volume of this gas animals can live longer than in the same volume of air.

From experiments such as above, Lavoisier in 1777 concluded that the air was made up of two gases, opposite in nature; one of them, present to the extent of about 20 per cent. by volume, capable of supporting and encouraging combustion and life; the other composing 80 per cent. of the atmosphere, incapable of supporting either combustion or life. The active

ELEMENT.	SOLID, LIQUID, OR GAS AT ORDINARY TEMPERATURES.	DENSITY AT ORDINARY TEMPERATURES.	GENERAL APPEARANCE.
Oxygen	Gas	[H=1] 16	Colourless, odourless, tasteless
Nitrogen	,,	,, 14	,, ,, ,,
Argon	,,	,, 20	,, ,, ,,
Hydrogen	,,	,, 1	,, ,, ,,
Chlorine	,,	,, 35·5	Greenish, pungent fumes
Carbon	Solid—non-metallic	(Water=1) diamond, 3·52 graphite, 2·2	Variable
Silicon	,, ,,	,, 2·34	
Sulphur	,, ,,	,, 2·1	Yellow; crystalline
Phosphorus	,, ,,	,, white, 1·83 red, 2·33	Yellow; waxy; fumes in air Red amorphous powder
Iodine	,, ,,	,, 4·94	Dark violet; crystalline
Sodium	Solid—metallic	,, 0·97	Very soft; greyish; soon tarnishes in air
Potassium	,, ,,	,, 0·875	Very soft; greyish
Calcium	,, ,,	,, 1·55	Bluish white resembling zinc
Magnesium	,, ,,	,, 1·74	Bright grey; soon tarnishes in air
Aluminium	,, ,,	,, 2·70	Greyish white
Zinc	,, ,,	,, 7·12	Bluish grey
Tin	,, ,,	,, 7·28	Silvery; fairly soft
Lead	,, ,,	,, 11·35	Bluish grey; soft; soon tarnishes
Silver	,, ,,	,, 10·50	Does not readily become dull
Gold	,, ,,	,, 19·27	Yellow; soft; heavy
Copper	,, ,,	,, 8·93	Reddish brown
Manganese	,, ,,	,, 7·39	Greyish white; brittle
Iron	,, ,,	,, 7·86	Dark grey
Platinum	,, ,,	,, 21·5	Soft; silvery; heavy
Bromine	Liquid—non-metallic	,, 3·19	Red; fuming; pungent
Mercury	Liquid—metallic	.. 13·6	Silvery liquid

or "good air" he called oxygen; the "bad air," nitrogen. The red particles were particles of mercuric oxide.

The experiment on p. 93 is one of many which may be made to verify Lavoisier's conclusions.

Oxygen, then, may be prepared by heating mercuric oxide. This, however, is a rather expensive process, and a commoner method of preparing the gas is to heat a mixture (known as oxygen mixture) of two substances—viz., potassium chlorate and manganese dioxide. The method of preparation is discussed more fully on p. 156. The apparatus required is shown in Fig. 58. On heating the mixture a gas is evolved which is collected over water in the jars. Several jars full of this gas (oxygen) may be obtained from a few grams of oxygen mixture. The oxygen may be tested in a variety of ways, when it will be found to have the following properties: Colourless, odourless, tasteless gas; not very soluble in water, does not burn in air, but substances which burn in air burn much more brightly in oxygen. A splint of wood only glowing in air will burst into flame when introduced into oxygen.

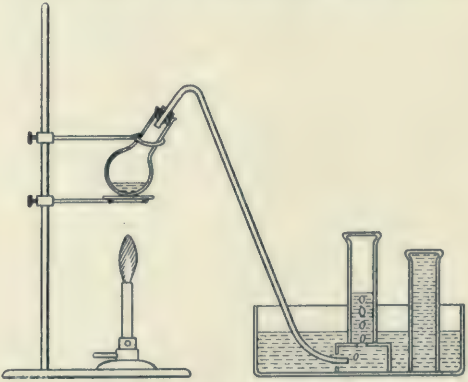

FIG. 58.—PREPARATION OF OXYGEN.

Nitrogen is usually prepared as the residual gas after the air has been deprived of its oxygen. The oxygen may be absorbed from a certain volume of air by means of phosphorus. It is preferable to ignite the phosphorus though the absorption of oxygen takes place slowly at ordinary temperatures. A more practical method of preparing nitrogen is to pass air over heated copper turnings contained in a hard glass tube (Fig. 59). The oxygen of the air combines with the copper, forming copper oxide, while the nitrogen passes out at the end of the tube, whence it may be conducted through a delivery tube and collected over water, as in the case of the oxygen.

On examining the gas it will be found that nitrogen is a colourless, odourless, tasteless gas, even less soluble in water than is oxygen. It does not burn nor support combustion, a burning taper being immediately extinguished on introduction into a jar of the gas. Nitrogen also does not support life, but it is not poisonous. It is a very inactive gas, and may be regarded principally as a diluent of the oxygen, as far as its function in the atmosphere is concerned.

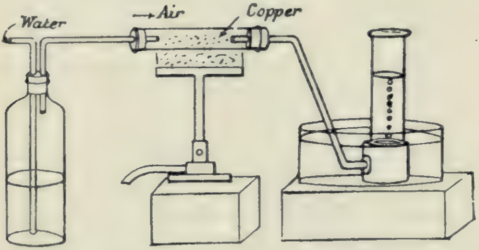

FIG. 59.—PREPARATION OF NITROGEN.

Liquefaction of Gases—Liquid Air.—Gases can be liquefied provided they are cooled below a certain *critical temperature* (which temperature varies considerably for different gases), and are at the same time compressed to the requisite degree.

The critical temperatures of a number of gases are given. Above these temperatures the gases cannot be liquefied by any pressure, however great.

Gas.	*Critical Temperature in Degrees Centigrade.*
Ammonia	130·0
Hydrochloric acid (gas)	52·3
Acetylene	37·0
Carbon dioxide	31·9
Ethylene	10·1
Methane	− 83·0
Oxygen	−119·0
Carbon monoxide	−140·0
Nitrogen	−146·0

In order to liquefy air, a very low temperature must be obtained. This is produced in the following manner: The air is first compressed in stages until it is under a great pressure. During this compression the air tends to become hot, but the heat is removed by surrounding the compressors with cold water jackets. Part of the air so compressed is now allowed to expand and escape, and in doing so it absorbs heat from the remainder of the compressed air which is cooled down further. The process is continued until the air is cooled sufficiently to liquefy it. Another method is first to liquefy some gas such as carbon dioxide by compression at ordinary temperatures. The liquid carbon dioxide may be stored in strong steel cylinders under pressure. Now, if some of the liquid carbon dioxide be allowed to evaporate by reducing the pressure, (latent) heat is absorbed, and by a suitable arrangement of apparatus the heat may be absorbed from a second gas which it is desired to cool. By this means a temperature sufficiently cold easily to liquefy ethylene may be obtained. If, in turn, ethylene be allowed to evaporate, a temperature low enough to permit of the liquefaction of oxygen may be produced. And if liquid oxygen be allowed to evaporate, a considerably lower temperature will be obtained, and so forth.

It is necessary in liquefying air first to filter it from mechanical impurities (dust, etc.), and also to remove the carbon dioxide, a trace of which is always present, by passing the air through a "caustic-soda tower."

Fig. 60 shows the apparatus employed by Wroblewski for liquefying oxygen. *A* is a steel cylinder in which the oxygen is contained under a pressure of 120 atmospheres. *B* is a strong glass vessel connected to *A* through a fine metal tube, and surrounded by a vessel *C* in which there is a small aperture *O*. *C* is in turn surrounded by a larger vessel which communicates with a vacuum air-pump. *D* contains liquid ethylene, and this is led via a spiral *S* (cooled in a mixture of ether and solid carbon dioxide) into tube *C*, where rapid evaporation is ensured by pumping off the vapour through the aperture *O*, and thence out of the largest vessel. The temperature so produced was below −150° C., and liquid oxygen was obtained in *B*.

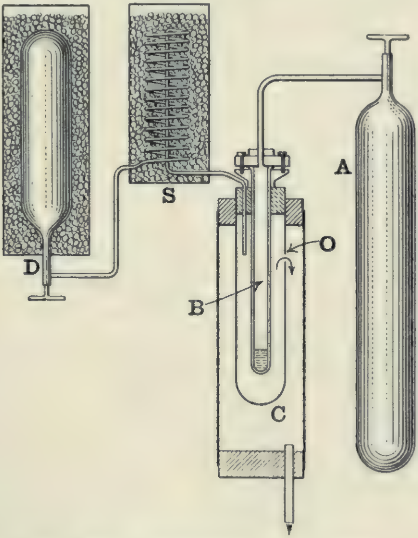

Fig. 60.—Wroblewski's Apparatus.

Air—A Mechanical Mixture, not a Compound.—The properties of air are the average of those of its constituents. Also, when these constituents are mixed in the proper proportions, the mixture so formed is indistinguishable from ordinary air, and there is no evidence (such as evolution or absorption of heat) of any chemical change taking place during the mixing. Finally, by mechanical means, air may be separated into its constituents. This is accomplished when the air is cooled down, compressed, and liquefied.

Liquid air so obtained is a pale blue liquid of about the same density as water. It does not all evaporate instantaneously in air, as the intense cold produced by the evaporation of part of the liquid air is sufficient to keep down the temperature and prevent the remainder from evaporating as rapidly as might be expected. The important point to notice, however, with regard to its indication that air is a mixture and not a compound is this—viz., that on evaporation the nitrogen evaporates more rapidly than does the oxygen. The last portions to evaporate are practically pure oxygen, and this fact is made use of in the manufacture of oxygen for commercial purposes.

Liquid air is used in certain types of *breathing apparatus for rescue work.* The liquid air so employed has a composition of about 60 per cent. oxygen and 40 per cent. nitrogen at the start, and as the work progresses the richness in oxygen increases. This is fortunate, as the oxygen is the necessary element for respiration. Moreover, the steady evaporation of the liquid air maintains a cool atmosphere in the apparatus, which is highly desirable. In order to obtain an even rate of evaporation and to prevent spilling, the liquid air is absorbed either in kieselguhr or in asbestos wool—both inorganic, mineral substances.

Liquid air, because of its high oxygen content, rapidly attacks organic materials such as rubber, oils, and the like, and it is usually stored in large metal vessels with evacuated jackets —*i.e.*, in large thermos-flasks which are left unstoppered. There is always some evaporation taking place, but if this is prevented enormous pressures are developed. The loss due to evaporation is not as serious as might be imagined at first, because, as has been stated, the intense cold produced when a little of the liquid air goes to the gaseous form appreciably slows down the rate of evaporation of the remainder.

Examination of Water.

Natural waters on evaporation yield more or less sediment according to their degree of purity. To obtain pure water, natural water is boiled, and the steam so formed is cooled down and condensed to water in a separate vessel, the sediment or impurities remaining in the original vessel. The process is known as distillation, and the apparatus required is shown in Fig. 61.

Preparation of Pure Water.—The water to be distilled is boiled in the flask *A*, and the steam given off passes through the inner tube of the Liebig's Condenser, *C*. In the outer jacket of the condenser cold water (impure water will do) is maintained in circulation, which brings about the rapid condensation of the steam in the inner tube of the condenser. The condensed or distilled water flows out and is collected in flask *B*. Except for certain refined work, the water thus obtained is pure enough for all practical purposes.

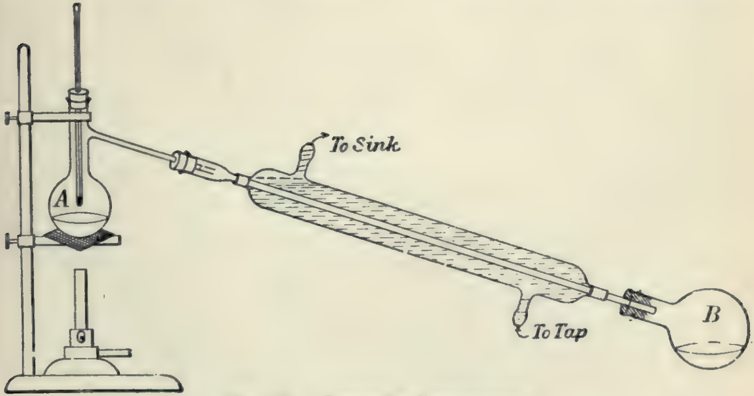

FIG. 61.—LIEBIG'S CONDENSER.

Properties of Water.—The physical properties of water are well known, but certain chemical properties may be noticed here. If a small piece of sodium (a metal) be thrown on to water, vigorous action takes place, the globule of the metal travelling about on the surface of the water with a hissing sound. If a lighted taper be brought near the sodium, the latter can apparently be ignited. It is possible, however, to show that it is not the sodium which is burning, but that the gas which is being liberated by the chemical action is combustible, and it is this gas (called hydrogen) which is burning. The gas may be collected in order to test this. (Certain precautions are necessary.) The **hydrogen** so obtained is found to be colourless, odourless, and tasteless. It is also exceptionally light, and when tested with a flame it either burns or explodes. Now, in the above experiment the hydrogen might have come from the sodium, or from the water, or from the air. We have seen, however, that the air consists of two gases—oxygen and nitrogen—and it is known that these gases are elements. Moreover, sodium is an element. It would therefore appear that this new gas must have come from the water.

Other metals, such as iron, magnesium, and zinc, do not split up water so readily at low temperatures, but when steam is passed over any of the above metals heated to redness, the same gas—hydrogen—is obtained (see p. 120, Figs. 67 and 68).

Hydrogen is usually prepared in other ways (see p. 119). It may be collected over water as in the case of oxygen, or it may be led to the top of an inverted jar and collected by its expelling the air downwards from the jar. If desired, the hydrogen may be lighted at a jet, but only after all the air has been displaced from the apparatus, otherwise there is danger of an explosion. Dry hydrogen burning at such a jet has a pale blue flame. If this flame is allowed to impinge on a cold surface drops of a clear liquid are formed (Fig. 62). On testing this liquid, it is found to be water. It may be tested for the following: colour, taste, smell, residue on evaporation, density, freezing-point, boiling-point, action with sodium, and in each case it will be found to have the properties of water. It may also be tested with white (anhydrous) copper sulphate, which is turned blue on the addition of water. From the above it would seem that hydrogen is contained in water, and this is true. It might also be concluded that as water is formed when hydrogen burns in air, the other constituents or constituent of water is present in the air. It has been seen that nitrogen is rather inactive, whereas oxygen is very energetic. It is probable, therefore, that water consists of hydrogen and oxygen, though, of course, at this stage it cannot be said that there is no nitrogen present. However, the question was settled many years ago. Cavendish, about 1800, found that hydrogen and oxygen alone will, on explosion, yield water, and Scheele had already shown that when hydrogen was burned in a closed space, one-fifth of the air was removed and the residue was nitrogen (Fig. 63). It is clear, then, that water is composed only of the two gases—hydrogen and oxygen—chemically combined together. One hundred cubic centimetres (about 6 cubic inches) of hydrogen at N.T.P. on burning will yield only a drop of water.

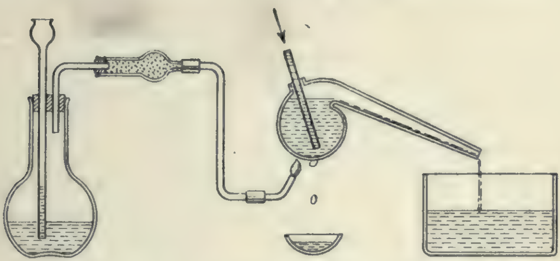

Fig. 62.—Burning of Hydrogen.

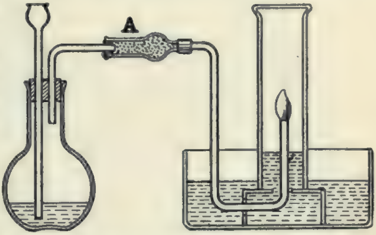

Fig. 63.—Hydrogen Burning in Closed Space.

Synthesis of Water.—On exploding mixtures of hydrogen and oxygen, the residual gas, after explosion, is always such as to show that 2 volumes of hydrogen have combined with 1 volume of oxygen. If excess of hydrogen (say 3 volumes) is used, the residual gas will be 1 volume of hydrogen. If excess of oxygen (say 3 volumes) is used, the residual gas will be 2 volumes of oxygen. Water is formed in every case, but its volume is so small as to be negligible. It has been seen how water may be split up by the action of metals, and also how it may be built up by exploding (most conveniently by means of an electric spark) together two gases—hydrogen and oxygen—but the following experiments should leave no uncertainty about the composition of water:

1. **Electrolysis of Water.**—If an electric current be passed through water (see p. 121) by means of a *voltameter* (see Fig. 64) two gases are given off, and they collect in the limbs of the "voltameter." One gas is given off at the positive electrode, +, and the other at the negative electrode, −. Moreover, there is twice the volume of gas liberated at the negative electrode that there is at the positive. On testing these gases, it is found that the larger volume of gas is hydrogen while the smaller is oxygen. Here, therefore, is another confirmation of the fact that water is composed of the two gases—hydrogen and oxygen—combined in the ratio of 2 volumes of hydrogen to 1 volume of oxygen. Now 1 litre of hydrogen weighs 0·09 gram and 1 litre of oxygen weighs 1·44 grams. The proportion by weight of hydrogen to oxygen in water is therefore 1·44 : 2 × 0·09 = 1·44 : 0·18 = 1 : 8. In other words, 1 gram of hydrogen combines with 8 grams of oxygen to form 9 grams of water.

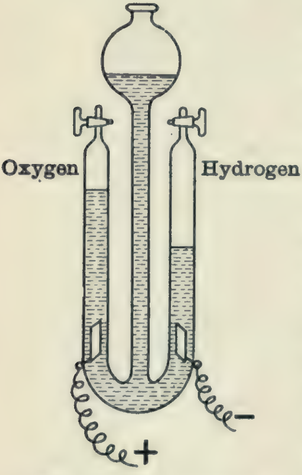

Fig. 64.—Voltameter.

2. **Dumas** verified this in the following manner: Hydrogen was passed over a certain weight of black copper oxide heated in a strong glass tube. Oxygen by this means is taken from the copper oxide and combines with the hydrogen to form steam which condenses to water. By a suitable arrangement

of apparatus Dumas absorbed all the water formed and weighed it (see Fig. 65). He likewise weighed the impure copper oxide left after the experiment. The loss in weight of the copper oxide represented the oxygen used to form the water. Dumas found that 9 grams of water were formed from 8 grams of oxygen. The difference, 1 gram, is clearly the weight of hydrogen.

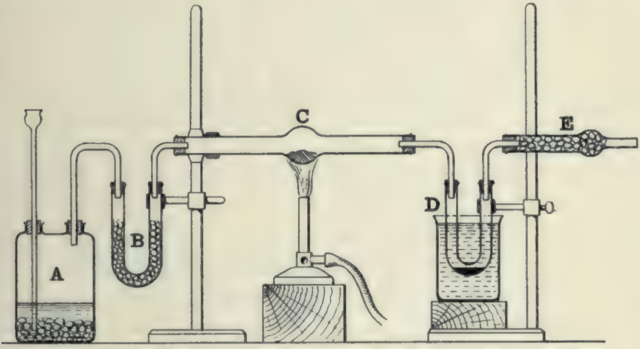

FIG. 65.—DUMAS'S EXPERIMENT.

Note.—In Dumas's actual experiment a large number of tubes were used for purifying the hydrogen and for absorbing the water.

Water—A Chemical Compound.—Water has always the same composition. Its properties are totally unlike those of its constituents, and when formed from its constituents there is physical evidence (in the form either of flame or of an explosion) of a chemical change. Moreover, water cannot, by easy mechanical means, be split into its constituents. It is therefore a chemical compound.

CHAPTER VIII

THE LAWS OF CHEMISTRY.*

ON analysing a number of chemical compounds one is first struck by the fact that every chemical compound has a very definite chemical composition. In every such compound there are always the same elements united in the same proportions (by weight), and from these experiments the **law of constant chemical composition** has been deduced. This law may be stated thus: "**In any particular chemical compound the same elements are always present united in the same proportions by weight.**" We have seen one instance of this law in the composition of water, where there is always present 8 parts by weight of oxygen combined with 1 part by weight of hydrogen. In black copper oxide, another chemical compound, there are 63 parts by weight of copper united with 16 parts by weight of oxygen to yield, of course, 79 parts by weight of copper oxide. In carbon dioxide there are 12 parts of carbon united with 32 parts of oxygen to every 44 parts of carbon dioxide. In methane there are 12 parts of carbon united with 4 parts of hydrogen to every 16 parts of methane, and so forth.

Equivalents.—The above figures are not expressed more or less at random. On re-examination it will be seen that the amounts of oxygen given are all divisible by 8, of carbon the amounts are 12 in each case, of hydrogen the least amount is 1 and the greatest is 4. Observe the following:

In water the ratio by weight of hydrogen to oxygen is 1: 8.
In carbon dioxide the ratio by weight of carbon to oxygen is 12: 32.
In methane the ratio by weight of carbon to hydrogen is 12: 4.

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* If the reader experiences difficulty with this chapter, it can be left until later chapters have been worked through.

It would seem from the above that the weights of substances which combine with one another are often the same weights which combine with 1 part by weight of hydrogen or 8 parts by weight of oxygen. This fact is confirmed by numerous analyses.

Hydrogen is chosen as unity on account of its being the lightest substance known. The equivalent weight of an element is defined as **that weight of the element which will combine with or replace 1 part by weight of hydrogen.** Some equivalents are given below:

Hydrogen = 1
Oxygen = 8
Carbon = 3
Copper = 31·5
Zinc = 32·6
Silver = 108

Law of Multiple Proportions.—There are several cases, however, where one element combines with another in more than one proportion by weight. It has been seen that 1 gram of hydrogen combines with 8 grams of oxygen to form 9 grams of water, but it is true also that under certain conditions another combination of hydrogen and oxygen may be formed in which 1 gram of hydrogen is united to 16 grams of oxygen to yield 17 grams of hydrogen peroxide. Similarly, we have carbon dioxide and carbon monoxide. In carbon dioxide there are 32 parts of oxygen combined with 12 parts of carbon, whereas in carbon monoxide only half the above 32—*i.e.*, 16 parts of oxygen—are combined with 12 parts of carbon. The ratio, however, is not always 2 or $\frac{1}{2}$, but it is always a very simple ratio.

From these and many other examples the Law of Multiple Proportions was evolved. It states: **"When one element unites with another element to form more than one compound, the weights of one element which combine with a fixed weight of the other element bear a simple relation to one another."**

It follows from the above that an element *may* have more than one equivalent. In such cases it is customary to consider only that equivalent found on analysis of the more common compounds.

Dalton's Atomic Theory.—To explain the facts noted above Dalton put forward a theory that all matter was composed of minute, **indivisible** particles called atoms, and he suggested that when chemical combination took place it did so in atoms. Now these particles, no matter how small, must have mass and weight. Consequently, the weights of substances taking part in a chemical change must be directly proportional to the weights of the atoms. For instance, 1 gram of hydrogen and 35·5 grams of chlorine unite under the influence of the electric spark to form 36·5 grams of hydrochloric acid. Now in hydrochloric acid 1 atom of hydrogen may be united to 1 or 2 or 3 or more atoms of chlorine. The simplest hypothesis is that 1 atom of hydrogen is united with 1 atom of chlorine, and this is found to agree with further evidence (see p. 109). If this is so, then, considering the weight of the hydrogen atom as unity, the weight of the chlorine atom must be 35·5. We cannot, by any known means, weigh the atoms themselves, but their weight can always be expressed as so many times the weight of the hydrogen atom. Recent research tends to modify the old conception of the atom, but for all except very specialised work the atom may be regarded as **"the smallest portion of an element which can take part in a chemical change."**

The next step is to find the number of atoms of each element present in any given compound containing hydrogen and so decide upon the atomic weight of the element in question. One method of approach is through Gay-Lussac's **Law of Volumes** as follows: It is observed from a number of experiments that **"when gases combine chemically, they do so in volumes which are in very simple ratio to one another, and also to the volume of the resulting product, if it be a gas."**

For instance:

2 volumes of hydrogen + 1 volume of oxygen yield 2 volumes of water (as steam).

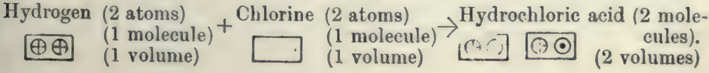
1 volume of hydrogen + 1 volume of chlorine yield 2 volumes of hydrochloric acid.

1 volume of carbon monoxide + 1 volume of oxygen yield 2 volumes of carbon dioxide.

The rule is true for all combinations of gases to form gaseous compounds, and Gay-Lussac first formulated the above law. It is, of course, understood that the pressure and temperature are kept constant throughout.

The conclusion first drawn from these observations was that equal volumes of gases contained the same number of atoms. Thus, considering the case of hydrogen and chlorine combining to form hydrochloric acid, it was thought that 1 atom of hydrogen combined with 1 atom of chlorine to form 2 atoms of hydrochloric acid. Now each atom of hydrochloric acid must contain at least 1 atom of hydrogen, for half-atoms do not exist. There is clearly some error. **Avogadro,** however, suggested the following satisfactory explanation, known as **Avogadro's Hypothesis.** Combination takes place, he said, among small groups of atoms, which groups he called molecules; and "**equal volumes of gases contain the same number of molecules.**" A **molecule** is defined as "**the smallest particle of a substance which can exist in the free state and which has the properties and composition of the substance.**" The number of atoms in a molecule of a substance depends, we now know, considerably on the temperature. The molecule of a substance as a solid as a rule contains more atoms than the molecule of the same substance as a liquid; and similarly the molecule of a liquid is more complex than that of a gas.

Avogadro's hypothesis explains the combination of 1 volume of chlorine with 1 volume of hydrogen to form 2 volumes of hydrochloric acid by assuming that the molecules of hydrogen and of chlorine contain 2—at least 2—atoms. It follows, therefore, that since the volumes of gases are as stated, the molecules are in exactly the same ratio—in other words, that 1 molecule of hydrogen combines with 1 molecule of chlorine to give 2 molecules of hydrochloric acid. Dividing the hydrogen and chlorine molecules into 2 atoms each, it is seen that 2 atoms of hydrogen combine with 2 atoms of chlorine to yield 2 molecules of hydrochloric acid. Diagrammatically—



Each hydrogen atom attaches itself to a chlorine atom, and the molecule of hydrochloric acid is the result of the combination. Observe, it is not correct to speak of the atom of hydrochloric acid, as hydrochloric acid is not an element.

Molecular Weights.—The weight of the **hydrogen atom** is taken as the **unit.** Since there are two atoms of hydrogen in the molecule (see p. 111), the weight of the hydrogen molecule is therefore 2. Now, by Avogadro's hypothesis, in equal volumes of gases (at the same temperature and pressure) there are the same number of molecules. If 1 cubic foot of hydrogen contains, say, one million molecules, then 1 cubic foot of oxygen, or of carbon dioxide, or of chlorine, or of any other gas, contains a million molecules. It follows, therefore, that the weights of 1 cubic foot of hydrogen, carbon dioxide, chlorine, etc. are representative of the weights of one million molecules of each. (One million is a purely imaginary number, millions of times too small, but the argument is none the less true.) The weights of a cubic foot of hydrogen, carbon dioxide, and chlorine are in the ratio 2 : 44 : 71. It follows, then, that the weights of the molecules are in the same proportion, and as the weight of the hydrogen molecule is 2, the weight of the molecule of carbon dioxide is 44, and that of chlorine is 71.

Similarly, since 1 litre (1,000 c.c.) of hydrogen (at N.T.P.) weighs 0·09 gram, and 1 litre of oxygen (at N.T.P.) weighs 1·44 grams, the molecular weight (x) of oxygen may be found as follows:

$$\frac{1{\cdot}44}{0{\cdot}09}=\frac{x}{2};\ x=\frac{2\times 1{\cdot}44}{0{\cdot}09}=32.$$

In oxygen, in hydrogen, in chlorine, and in most **elementary** gases (carbon dioxide is not an elementary but a **compound** gas) there are 2 atoms in the molecule. It follows that the weight of the oxygen atom is $\frac{32}{2}=16$, that the weight of the chlorine atom is $\frac{71}{2}=35{\cdot}5$. (See Atomic Weights, p. 111.)

It should be clear from the above that if we take such weights of two gases, say hydrogen and oxygen, as are in proportion to their molecular weights, the volumes of such gases will be equal. For instance, 2 grams of hydrogen will have the same volume as 32 grams of oxygen, or as 71 grams of chlorine.

Now 2 grams of hydrogen at N.T.P. have a volume of 22·4 litres.
∴ 32 grams of oxygen at N.T.P. have a volume of 22·4 litres.
∴ 71 grams of chlorine at N.T.P. have a volume of 22·4 litres.
∴ 44 grams of carbon dioxide at N.T.P. have a volume of 22·4 litres.
∴ 16 grams of methane at N.T.P. have a volume of 22·4 litres (molecular weight of methane = 16).
∴ 28 grams of nitrogen at N.T.P. have a volume of 22·4 litres (molecular weight of nitrogen = 28).

In other words, **the molecular weight of any gas in grams has a volume of 22·4 litres at N.T.P.**

Density of a Gas.—Hydrogen is taken as the standard. The density of a gas is defined as the number of times it is heavier than hydrogen, volume for volume. The molecular weight of any gas is clearly twice its density, since the molecular weight of hydrogen is 2.

The **Specific Gravity of a gas** is the number of times it is heavier than air, volume for volume.

Atomic Weights.—The evidence for the fact that there are two atoms in the molecules of the elementary gases considered is further supported by experiments of a physical nature. These are connected with the ratio of the specific heat of the gas at constant volume to the specific heat of the gas at constant pressure, but this is beyond our scope.

Careful work shows that if the molecular weight of hydrogen be taken as 2, the molecular weight of oxygen is not quite 32, but 31·76. This would make the atomic weight of oxygen 15·88. It is, however, customary to regard the atomic weight of oxygen as 16 and that of hydrogen as 1·008. This is convenient because of the large number of compounds which contain oxygen. Atomic weights may be obtained as follows:

1. It has been seen how the atomic weights of gaseous elements may be found by halving their molecular weights, which, in turn, may be found by weighing a known volume of the gas at known temperature and pressure.

2. To find the atomic weight of an element not easily obtained in the form of a gas, but which forms gaseous compounds with other elements, the gaseous compounds are analysed, and their molecular weights found by weighing known volumes of the gases as above. On examination of a number of these analyses, the smallest weight of the element present in any molecule is taken as the atomic weight of the element—*e.g.*, carbon forms many gaseous compounds:

	Molecular Weight.	*Percentage Carbon by Weight.*	*Weight of Carbon in the Molecular Weight.*
Carbon monoxide..	28	42·9	12·0
Carbon dioxide ..	44	27·3	12·0
Methane	16	75·0	12·0
Ethane	30	80·0	24·0
Propane	44	81·8	36·0

A figure less than 12 has never been obtained for the weight of carbon in the molecular weight of any carbon compound. The atom of carbon has therefore a weight of 12.

Note.—The molecular weights of the compounds may be determined (if they are not gaseous) by noting how much the freezing-point of a liquid is lowered or the boiling-point raised when a certain weight of the compound is dissolved in the liquid. The method is based upon the fact that in dilute solutions of any particular liquid the freezing-point of the liquid is lowered by the same amount by the same number of molecules of different substances. The boiling-point is raised in a similar manner to a certain degree by equal numbers of molecules of different substances.

3. Another method of ascertaining the atomic weight of an element is based upon the fact that the "equivalent" (see p. 106) of an element is either the same as its atomic weight or is a simple multiple of it. Thus, since the equivalent of oxygen is 8, the atomic weight of oxygen is either 8 or 16 or 24 or 32, etc. It cannot be less than 8. A few more examples are given:

Element.	*Equivalent.*	*Atomic Weight.*
Hydrogen	1·0	1·0
Chlorine	35·5	35·5
Copper	31·8	63·6
Carbon	3·0	12·0

The equivalents of various elements can be found by analysis. In order to find out how many times the equivalent is contained in the atomic weight we may make use of the **Law of Dulong and Petit**, which states that the atomic weight of an element × its specific heat = 6·4 (approximately). This law was discovered from a number of observations of the above scientists. It signifies that any atom requires exactly as much heat to raise its temperature by a certain amount as does any other atom of a different element.

E.g., the equivalent of copper is 31·8. What is the atomic weight of copper, the specific heat of copper being 0·1 calorie per gram?

Atomic weight $= \frac{6\cdot4}{\text{specific heat}} = \frac{6\cdot4}{0\cdot1} = 64$, but this is only approximate.

The accurate atomic weight is clearly twice the equivalent $= 31\cdot8 \times 2 =$ **63·6.**

Valency.—The valency of an element

$$= \frac{\text{atomic weight of the element}}{\text{equivalent weight of the element}}.$$

And since an element may have more than one equivalent, so it may have more than one valency. The valency of hydrogen is 1, hydrogen having only one equivalent and one atomic weight. Now in hydrochloric acid 1 gram of hydrogen is combined with 35·5 grams of chlorine. The equivalent of chlorine is therefore 35·5. But it is found that the atomic weight of chlorine is 35·5. It follows that the valency of chlorine is $\frac{35\cdot5}{35\cdot5}=1$.

In water, as 1 part by weight of hydrogen is combined with 8 parts by weight of oxygen, the equivalent of oxygen is 8· The atomic weight of oxygen, however, is 16. The valency of oxygen is therefore $\frac{16}{8}=2$. And as there cannot be less than one atom of oxygen in the molecule of water, it follows that there must be 16 parts of oxygen by weight (atomic), which will require 2 parts of hydrogen by weight—*i.e.*, 2 atoms of hydrogen, since the weight of the hydrogen atom is taken as 1. In water, therefore, 2 atoms of hydrogen are united to 1 atom of oxygen. In ammonia it may similarly be shown that 1 atom of nitrogen is combined with 3 atoms of hydrogen. The valency of nitrogen in this case is therefore 3. A list of the commoner elements and their usual valencies is given below. Several elements will be observed to have two or more valencies. In monovalent elements it is common to imagine the atom of the element capable of throwing out only one bond; in divalent elements two bonds; in trivalent elements three bonds, and so forth (see p. 115, graphical formulæ).

COMMON VALENCIES OF DIFFERENT ELEMENTS.

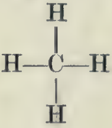
Monovalent. 1	*Divalent.* 2	*Trivalent.* 3	*Quadrivalent.* 4	*Pentavalent.* 5	*Hexavalent.* 6	*Heptavalent.* 7	*Octavalent.* 8
Hydrogen	Oxygen	Nitrogen	—	Nitrogen	Sulphur	Manganese	Osmium
Chlorine	Calcium	Phosphorus	Carbon	Phosphorus			
Sodium	Zinc	Arsenic	Silicon	Arsenic			
Potassium	Lead	Antimony	Sulphur	Antimony			
Silver	Iron	Iron	Lead				
Copper	Copper	Aluminium	Tin				
Gold	Tin	Gold	Platinum				

Symbols and Formulæ.—The atoms of the various elements are denoted by various symbols. A list of the atomic weights of the elements and their symbols is given in the Appendix. The symbol is sometimes the first letter of the word denoting the element; sometimes the first letter of the Latin name for the element, as in sodium, Na (natrium), and potassium, K (kalium). This is in order to distinguish them from sulphur (S) and phosphorus (P). The true use of the symbol, therefore, is to denote *one atom* of the element in question, but it is convenient often to use the symbol merely to indicate the element without any reference to its atomic form. This, however, should not be done in writing chemical equations.

A chemical formula for a compound is written with the symbols of the component elements. The number of atoms of any particular element present is indicated by a small figure placed immediately after the element. The strict use of the formula is to indicate one molecule of the substance, but a similar latitude is allowed to that mentioned above in the case of the symbols denoting not necessarily the atomic form. Thus, the molecule of water is written H_2O, indicating that it is composed of 2 atoms of hydrogen combined with 1 atom of oxygen. The molecule of carbon dioxide is written CO_2, indicating that it is made up of 1 atom of carbon and 2 atoms of oxygen.

Radicles.—A group of elements acting as though it were one element is called a "radicle." Thus, all carbonates contain the CO_3 group; all sulphates the SO_4 group; all ammonium compounds the NH_4 group; all nitro-compounds the NO_2 group; and so forth. These radicles have valencies; CO_3 is divalent; SO_4 is divalent; NH_4 is monovalent; NO_2 is monovalent; NO_3 is monovalent.

Graphical Formula.—Hydrochloric acid is indicated commonly by the formula HCl. Graphically this might be written H—Cl, with a link or bond joining the H and the Cl. This link is formed of two small links; one from the H and one from the Cl. If the elements had been divalent, they would have sent out two small links each. And if one of the elements had been divalent and the other monovalent, as in water (H_2O), the links would have arranged themselves as in the formula H—O—H. Observe in such a case it requires two atoms of the monovalent element to combine with one atom of the divalent. For methane, CH_4, the graphical formula becomes—



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

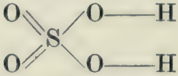
carbon being quadrivalent.

For carbon dioxide, CO_2, the graphical formula is—

$$O=C=O,$$

oxygen being divalent and carbon quadrivalent.

Sulphuric acid, H_2SO_4, written graphically, becomes—



sulphur being in this case hexavalent.

Graphical formulæ are of great service in organic chemistry, where it frequently happens that many substances (known as isomeric substances) have the same composition, but are entirely different in their constitution—*i.e.*, in the arrangement of the atoms in the molecule. They consequently have entirely different properties.

Chemical Equations and Calculations.—The course of a chemical action can usually be conveniently indicated by an equation. In writing such equations molecular quantities should be present on each side of the equation, especially if there are any gaseous products indicated.

E.g.: 1. Mercuric oxide, on heating, yields oxygen and mercury.

The equation denoting the change is—

$$2HgO = 2Hg + O_2,$$

and *not*

$$HgO = Hg + O.$$

Further, the atomic weight of mercury (Hg) is 200.

And the atomic weight of oxygen is 16.

From the above equation it follows that 2 (200 + 16) parts by weight of mercuric oxide will yield 2 × 200 parts by weight of mercury and 2 × 16 parts by weight of oxygen.

2. When sulphuric acid (H_2SO_4) acts on zinc (Zn), hydrogen is evolved and zinc sulphate ($ZnSO_4$) formed.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Now the atomic weight of zinc is 65·4.

And the atomic weight of sulphur is 32.

It therefore follows that the parts by weight acting are (65·4) of zinc + (2 + 32 + 64) of sulphuric acid = (65·4 + 32 + 64) of zinc sulphate + (2) hydrogen.

These parts by weight may be in pounds or in ounces or in grams. If the weights are in grams it will be seen that 65·4 grams of zinc yield 2 grams of hydrogen or 22·4 litres of hydrogen at N.T.P. (see p. 111). In engineering units, 2·29 ounces of zinc yield 0·79 cubic foot of hydrogen at 32° F. and 30″ barometer when treated with excess of acid.

3. When limestone ($CaCO_3$) is heated strongly, carbon dioxide (CO_2) is given off, and quicklime (CaO) is produced. The equation denoting the change is:

$$CaCO_3 = CaO + CO_2.$$

The atomic weight of calcium (Ca) is 40.

The atomic weight of carbon (C) is 12.

It follows that—

(40 + 12 + 48) lbs. of limestone yield (40 + 16) lbs. of lime and (12 + 32) lbs. of carbon dioxide.

I.e., 100 lbs. of limestone yield 56 lbs. of quicklime.

4. What is the formula for benzene if the percentage carbon is 92·31, the percentage hydrogen 7·69, and the vapour density 39? (Given atomic weight of carbon = 12; hydrogen = 1.)

Molecular weight = 2 × vapour density = 2 × 39 = 78.

∴ Weight of carbon in 78 parts by weight of benzene

$$=\frac{92\cdot31\times78}{100}=72\cdot0,$$

and weight of hydrogen in 78 parts by weight of benzene

$$=\frac{7\cdot69\times78}{100}=6\cdot0.$$

∴ In one molecule of benzene—

$$\left.\begin{array}{ll}\text{Number of carbon atoms} & =\frac{72}{12}=6 \\ \text{and \quad ,, \quad ,, hydrogen ,,} & =\frac{6}{1}=6\end{array}\right\}\therefore\ \text{formula}=C_6H_6.$$

CHAPTER IX

Hydrogen.

Symbol = H; atomic weight = 1; molecular weight = 2; density = 1; specific gravity (air = 1) 0·07.

Occurrence.—Hydrogen very rarely occurs free, though it is probable that the uppermost reaches of the atmosphere contain a fair amount of the gas. Combined hydrogen, however, occurs in enormous amounts, in water, in animal and vegetable matter, in mineral oils, coal, etc.

Preparation.—1. By the action of a dilute mineral acid on a metal (nitric acid is not used, nor are the heavy metals, such as copper and lead). Zinc and dilute sulphuric acid are convenient:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

If dilute hydrochloric acid is used, the equation then becomes—

$$Zn + 2HCl = ZnCl_2 + H_2.$$

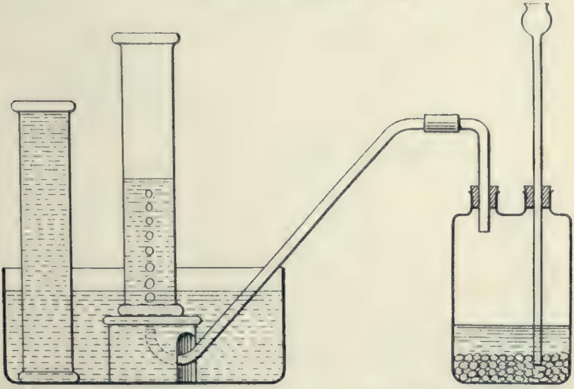


FIG. 66.—PREPARATION OF HYDROGEN.

The apparatus used is shown in Fig. 66. First cover the metal in the bottle with water, and then add a little sulphuric acid through the thistle funnel. Several jars of the gas are collected over water in the manner shown, neglecting the first jar as it contains much air from the apparatus. Zinc sulphate is left in the solution in the two-necked bottle.

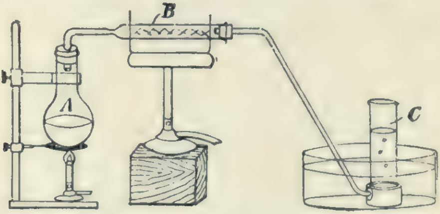


Fig. 67.—Action of Steam on Iron.

2. By passing steam over a heated metal, such as iron, zinc, or magnesium . If zinc is used:

$$Zn + H_2O = ZnO + H_2.$$

If iron is used:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

If magnesium is used:

$$Mg + H_2O = MgO + H_2.$$

In each case the oxide of the metal is formed.

The apparatus employed is shown in Fig. 67.

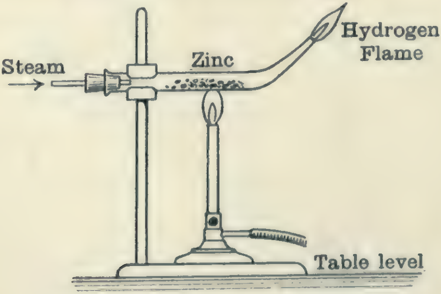


Fig. 68.—Action of Steam on Zinc.

The hydrogen may be burned at a jet (Fig. 68) and the liquid formed will, on testing, be found to be water (see p. 102).

3. By the action of sodium on water (see p. 101) hydrogen is liberated and a solution is formed which is alkaline—*i.e.*, is capable of neutralising acids, and turns red litmus blue.

$$2Na + 2H_2O = \underset{\substack{\text{Sodium hydroxide} \\ \text{or caustic soda}}}{2NaOH} + H_2.$$

4. By the electrolysis of water (see p. 104).

In this case the current is passed through water to which a drop of sulphuric acid has been added in order to make the liquid a better conductor. The same amount of sulphuric acid is present both before and after the experiment, showing that it is only the water which has yielded the gases.

$$2H_2O = 2H_2 + O_2.$$

Properties.—Hydrogen, when pure, is a very light, colourless, tasteless, odourless gas. It is not poisonous. It burns in air with a blue non-luminous flame which is exceptionally hot. This fact is made use of in the Clowes' Hydrogen Lamp for the detection and estimation of inflammable gas in small amounts in air (see p. 187). Commercially, the same fact is made use of in the oxyhydrogen blowpipe, in which a current of oxygen is forced through burning hydrogen. A temperature of 2,200° C. can be attained in this way. Hydrogen is also used on a large scale for filling balloons and airships, due to its lightness.

Hydrogen combines with explosive violence with oxygen in the proportions, by volume, of 2 : 1; by weight, of 1 : 8.

$$2H_2 + O_2 = 2H_2O.$$

Hydrogen is a powerful "**reducing agent.**" This means that when hydrogen acts on a compound it reduces the amount of oxygen in the compound, which it usually does by combining with the oxygen to form water. For instance, in Dumas's experiment (p. 105) hydrogen reduced black copper oxide to copper:

$$CuO + H_2 = Cu + H_2O.$$

Reduction, however, is in chemistry also regarded in a more general sense, and comprises (1) reactions in which the proportion of non-metallic elements in a compound are reduced; (2) reactions in which the proportion of oxygen is reduced; (3) reactions in which the proportion of hydrogen is increased.

Certain metals, such as platinum, palladium, and nickel, absorb or, more correctly, "occlude" hydrogen. The "occlusion" is most rapid and efficient when the metals are in a state of fine division.

Hydrogen is the necessary constituent of all acids, though all substances containing hydrogen are by no means acids. The hydrogen of an acid must be replaceable by a metal, as in the case where sulphuric acid acts upon zinc:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

The hydrogen of the acid is liberated and replaced by the zinc to form zinc sulphate.

Diffusion of Gases.

It is common experience that gases diffuse. If the coal-gas tap be left open and the gas be not lit, the coal-gas can be smelt after a while at quite a considerable distance from the burner. This is due to the "diffusion" or rapid wandering of the gas in all directions. The kinetic theory of gases states that the molecules of a gas are in a state of rapid motion, each molecule flying hither and thither until opposition is met when, nothing daunted, it rebounds with the self-same velocity and continues its travels. Clearly, if two gases are in contact the molecules of the one will soon be well mixed up with the molecules of the other. In other words, the gases will soon diffuse one into the other.

Rate of Diffusion—Graham's Law.—It is found by experiment that different gases diffuse at different rates. This might have been expected. It has been seen that the molecules of some gases are much heavier than the molecules of other gases, and the heavier molecules are naturally more sluggish in their movements than the lighter ones. The exact relationship, however, between their speed and their weight (or, rather, their *mass*) was discovered by Graham, who stated it thus:

"The rate of diffusion of a gas is inversely proportional to the square root of its density." (The density of any gas is always half of its molecular weight. It follows, therefore, that the speed of the molecules is inversely proportional to the square root of their weight.) The law as enunciated by Graham may be made clearer by the following example:

The densities of hydrogen, methane, oxygen, sulphuretted hydrogen, and carbon dioxide are respectively 1, 8, 16, 17, and 22.

Compare their rates of diffusion:

$$H : CH_4 : O : H_2S : CO_2 = \frac{1}{1} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{16}} : \frac{1}{\sqrt{17}} : \frac{1}{\sqrt{22}}$$
$$= 1 : \frac{1}{2{\cdot}83} : \frac{1}{4} : \frac{1}{4{\cdot}12} : \frac{1}{4{\cdot}69}.$$

Therefore, while 1 cubic foot of hydrogen would diffuse into air, say, in a given time, only $\frac{1}{2{\cdot}83}$ of a cubic foot of methane would diffuse into air in the same time; and only $\frac{1}{4{\cdot}69}$ of a cubic foot of carbon dioxide would diffuse into air in the same time.

To demonstrate the difference in the rates of diffusion of hydrogen into air and of carbon dioxide into air, the diffusion is allowed to take place through the walls of an unglazed earthenware vessel. The effect of gravity on the gases is eliminated by placing the lighter gas above the heavier, so that any mixing is due entirely to the process of diffusion. The apparatus used consists of a two-necked bottle containing coloured water with tubes as shown (see Fig. 69), one tapering to a jet and the other leading into the porous earthenware vessel through a rubber stopper. A beakerful of hydrogen is collected and placed over and round the porous pot, which at the start contains air. Water is forced out at the jet. The beaker may then be removed and the bottle inclined so that the end of the tube leading to the porous pot is under the water. The water will be seen to rise in the tube. The dotted lines indicate the best position for the pot and beaker if carbon dioxide is being used in place of hydrogen. (Carbon dioxide is much heavier than air, while hydrogen is much lighter.) In this case the water first rises in the tube leading to the pot, but on removing the beaker of carbon dioxide the water is forced down in this tube and begins to rise in the tube with the jet.

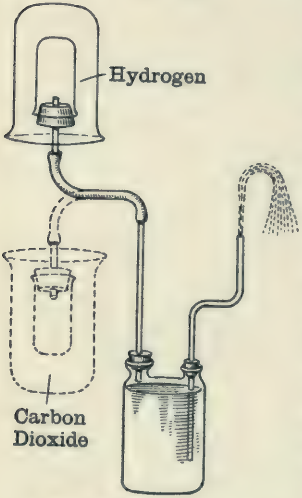


FIG. 69.—DIFFUSION EXPERIMENT.

The above observations are explained as follows: In the case of the hydrogen, the molecules of hydrogen are so active in their movements that in their rushing through the walls of the porous pot they choke the pores and prevent most of the air from escaping. This causes an increase in pressure inside the pot, which pressure is transmitted to the water and results in the forcing out of the water at the jet. On removing the beaker, the hydrogen now in the pot is as anxious as before to mix with the air, and the molecules of hydrogen again choke the pores of the pot by their outrush, and prevent the air from entering. A reduction in pressure follows, which is indicated by the rising of the water in the tube leading to the porous pot. In the case of the carbon dioxide the above effects are present in the reverse order, because of the fact that carbon dioxide is about one and a half times as heavy as air, and consequently diffuses much more slowly. The student should explain for himself the observations as noted.

Application.—Oxygen is a little heavier (denser) than nitrogen, their densities being respectively 16 and 14, but in the atmosphere, owing to the diffusion of the two gases, there is always present, by volume, 21 parts of oxygen and 79 parts of nitrogen.

Methane is a light gas, a little more than half as heavy as air. It is the principal constituent of firedamp, and in the mine, while it *tends* to collect in the rise workings, in cavities in the roof, at the face of the ripping (in the kenches), a certain amount of diffusion of the gas into the air current is continuously taking place. Often, however, it is necessary to direct the air current towards the roof by a suitable arrangement of brattice cloths or canvas before the gas can be effectively removed; but once the gas is dislodged, it soon mixes evenly with the air current, and the dilution with the ventilating current is usually sufficient to render the mixture non-explosive.

Carbon dioxide, a constituent of blackdamp and afterdamp, on the other hand, being a heavy gas, *tends* to accumulate in the dip workings and, if present in quantity, is not usually so readily dislodged as is methane. Moreover, it is characteristic of the gas to lie in a body beneath a moving current of air. These properties are due to its slow rate of diffusion.

In building stoppings or dams for isolating an underground fire, sand and much porous material are often used. It is often impossible to build a stopping in a mine gas-proof, and the probability of diffusion of carbon monoxide (whitedamp) and other associated gases through the dams into the fresh air current must always be borne in mind.

An instrument (Ansell's Firedamp Detector) for indicating small amounts of inflammable gas has been devised, based on the principle of the rate of diffusion of methane, but use of the apparatus is very limited. (See *Detection of Inflammable Vapour*, by Clowes and Redwood, published by Crosby Lockwood.)

Acids, Bases, and Salts.

When sulphur burns on air it forms an oxide, sulphur dioxide (see p. 205), which dissolves in water to form sulphurous acid. Sulphurous acid, on standing in air, gradually changes to sulphuric acid:

$$\underset{\text{Sulphur}}{S} + O_2 = \underset{\text{Sulphur dioxide}}{SO_2} \qquad SO_2 + H_2O = \underset{\text{Sulphurous acid}}{H_2SO_3}$$

$$2H_2SO_3 + O_2 = \underset{\text{Sulphuric acid}}{2H_2SO_4}.$$

In general, when non-metals burn in air or oxygen they yield an oxide which is acidic, often dissolving in water to give an acid.

Acids may be solids or liquids or gases; they are sour to the taste (*acidus* = sour); they all contain hydrogen, which is replaceable by a metal; they redden blue litmus (a vegetable colouring matter). They do *not* necessarily contain oxygen (*e.g.*, HCl—hydrochloric acid). The commoner and more important acids are:

1. Mineral acids—viz.:

Sulphuric acid (H_2SO_4).
Hydrochloric acid (HCl).
Nitric acid (HNO_3).

2. Organic acids:

Formic acid ($H.COOH$).
Acetic acid ($CH_3.COOH$).

Carbonic acid is a solution of CO_2 in water, and may be written H_2CO_3.

Bases are usually oxides or hydroxides of metals. They neutralise acids, forming only a neutral substance (called a salt) and water. *E.g.:*

$$\underset{\substack{\text{Caustic soda or}\\\text{sodium hydroxide}\\\text{(a base)}}}{2NaOH} + H_2SO_4 = \underset{\substack{\text{Sodium sulphate}\\\text{(a salt)}}}{Na_2SO_4} + 2H_2O.$$

Bases, or **alkalies,** as they are sometimes called, turn red litmus blue. In neutralising acids it is common to employ some such indicator as litmus in order to determine when a sufficient quantity of the alkali has been added.

Some of the commoner bases are:

Sodium hydroxide ($NaOH$).
Potassium hydroxide (KOH).
Calcium hydroxide ($Ca(OH)_2$).
Ammonium hydroxide (NH_4OH).

Salts.—It has been seen that a salt is formed when an acid is "neutralised" by a base, or when an acid acts upon a metal, as in the case of the salt zinc sulphate, formed by the action of sulphuric acid on zinc.

A salt may be defined as "the substance produced when part or all of the hydrogen of an acid is replaced by a metal." Sometimes in a salt not all the hydrogen of the acid is replaced, as in the case of sodium hydrogen sulphate, $NaHSO_4$. These salts are often called "acid" salts or "bi" salts. Thus $NaHSO_4$ is acid sodium sulphate, or sodium hydrogen sulphate, or sodium bisulphate.

Sulphuric acid (H_2SO_4) yields sulphates such as $(NH_4)_2SO_4$, $CaSO_4$, etc.

Hydrochloric acid (HCl) yields chlorides such as $NaCl$, $MgCl_2$, etc.

Nitric acid (HNO_3) yields nitrates such as $NaNO_3$, NH_4NO_3, etc.

Carbonic acid (H_2CO_3) yields carbonates such as $CaCO_3$, Na_2CO_3, etc.

Where only part of the replaceable hydrogen of an acid is replaced by a metal, "acid" or "bi" salts are produced. Thus:

1. $NaHSO_4$, sodium hydrogen sulphate, is also called acid sodium sulphate or sodium bisulphate; and
2. $NaHCO_3$, sodium hydrogen carbonate, is also called sodium bicarbonate.

Sulphuric Acid, H_2SO_4.

The crude commercial product is known as Brown Oil of Vitriol (B.O.V.).

Manufacture.—1. The principle of the process consists in oxidising sulphur dioxide by means of nitric acid fumes. Nitric acid is a substance rich in oxygen, and under certain conditions it readily parts with its oxygen to other bodies with which it is in intimate contact. The nitric acid is obtained by heating Chile saltpetre ($NaNO_3$) with a little sulphuric acid, and the sulphur dioxide is obtained by burning pyrites, FeS_2—

$$\underset{\text{Pyrites}}{4FeS_2} + 11O_2 = \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{8SO_2} + \underset{\text{Iron oxide}}{2Fe_2O_3}$$

$$\underset{\substack{\text{Chile saltpetre or}\\\text{sodium nitrate}}}{2NaNO_3} + H_2SO_4 = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\text{Nitric acid}}{2HNO_3}$$

The nitric acid (in the form of fumes) and sulphur dioxide are then brought into contact with each other, and steam is blown into the chamber at the same time.

Sulphuric acid is formed. The changes are complex, but they may be roughly denoted by the equation:

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + \underset{\text{Nitric oxide}}{2NO}.$$

The nitric oxide is not wasted, but is oxidised by the oxygen of the air into a form in which it may oxidise some further sulphur dioxide into sulphuric acid. The above process is known as the Lead Chamber Process, the acid being manufactured in leaden chambers.

2. A second process for the manufacture of sulphuric acid is known as the Contact Process. Sulphur dioxide and air are passed over heated platinum (in a fine and *special* form known as platinised asbestos), and the sulphur trioxide so formed is absorbed in 97 to 98 per cent. sulphuric acid. If this acid is not continually diluted, " oleum " or fuming sulphuric acid is produced. The acid is therefore kept down to the proper strength by means of a stream of more dilute acid run into the condensing tanks at the proper rate. This process is especially suitable for the manufacture of fuming sulphuric acid or " oleum."

Properties.—Sulphuric acid is a heavy, oily, colourless, odourless liquid, boiling at 338° C. It mixes with water in all proportions, and when poured into water great heat is developed, so that caution is necessary. It is very hygroscopic, picking up moisture from the air rapidly. It is therefore often used in desiccators and, in general, as a drying agent. Sulphuric acid is a very corrosive acid and rapidly attacks most metals (except lead and the noble metals). It chars or burns such organic materials as paper, cloth, wool, wood, sugar, etc. It is used in most chemical industries, especially in the dyeing industry and in the manufacture of explosives.

In mine waters sulphuric acid is sometimes found, its presence being due, usually, to the weathering and oxidation of pyrites or " brasses " (see pp. 143, 211).

Sulphuric acid is used in the manufacture of hydrochloric and nitric acids.

Hydrochloric Acid, HCl.

The aqueous solution of hydrochloric acid is known as Muriatic Acid or as Spirits of Salt.

Manufacture.—Common salt is heated with sulphuric acid. Fumes of hydrochloric acid are given off which are condensed in water to yield a convenient solution of the gas. The reactions which take place may be indicated in two steps:

$$1.\ \underset{\substack{\text{Common salt}\\ \text{or sodium}\\ \text{chloride}}}{NaCl} + H_2SO_4 = \underset{\substack{\text{Sodium}\\ \text{hydrogen}\\ \text{sulphate}}}{NaHSO_4} + HCl$$

$$2.\ NaHSO_4 + NaCl = \underset{\text{Sodium sulphate}}{Na_2SO_4} + HCl.$$

Properties.—Hydrochloric acid is a colourless gas with a characteristic pungent smell and bitter taste. It is very soluble in water, one volume of water dissolving about 500 volumes of the gas at ordinary temperatures, and the aqueous solution of the gas is now very often termed hydrochloric acid in the laboratory. The yellow colour of the commercial solutions of hydrochloric acid is due to a little impurity, such as a trace of iron. Hydrochloric acid attacks most metals (except gold and platinum) to form chlorides and liberate hydrogen. It is a most valuable chemical reagent.

$$Zn + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2.$$

$$Fe + 2HCl = \underset{\text{Ferrous chloride}}{FeCl_2} + H_2.$$

Like any other mineral acid it decomposes a carbonate, yielding carbon dioxide.

$$\underset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3} + 2HCl = \underset{\substack{\text{Calcium}\\ \text{chloride}}}{CaCl_2} + H_2O + \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{CO_2}.$$

Nitric Acid, HNO_3.

Also known as Spirits of Nitre and as Aqua Fortis.

Manufacture.—1. Chile saltpetre (sodium nitrate) is heated with sulphuric acid and the fumes given off are condensed.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

Cast-iron retorts are commonly used. In the laboratory the process may be imitated as shown in Fig. 70, the nitrate and sulphuric acid being heated in the retort.

2. In nitric acid are present three elements occurring in the atmosphere—viz., nitrogen, oxygen, and hydrogen. (The hydrogen in the air is combined as water vapour.) When an electric arc is passed through air, a small part of the oxygen and nitrogen combine to form nitric oxide (NO), and this gas, NO, immediately combines with more of the oxygen to form NO_2, nitrogen peroxide. NO_2, if dissolved in a little water, yields a mixture of nitrous and nitric acids.

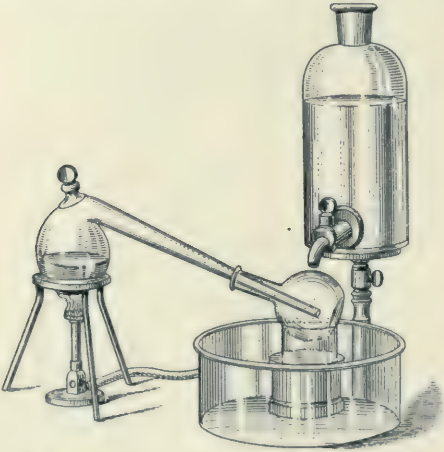


FIG. 70.—PREPARATION OF NITRIC ACID.

$$2NO_2 + H_2O = \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Nitrous acid}}{HNO_2}.$$

The above is the principle of some of the latest processes for the "fixation of atmospheric nitrogen," and is one way of making nitric acid. As a large amount of electrical power is required, many of the plants are situated near large waterfalls—*e.g.*, Niagara. The acids obtained are often neutralised with lime and the product evaporated to yield fertilisers, such as nitrolim, calcium nitrate, etc.

Properties.—Pure nitric acid is a colourless fuming liquid of specific gravity about 1·5. It attacks most metals violently, but unlike hydrochloric and sulphuric acids it does not, as a rule, evolve hydrogen, but rather oxides of nitrogen. This is due to its strong oxidising action, any hydrogen formed being oxidised to water. The following equations represent the actions of the acid on the metals copper and zinc:

$$3Cu + 8HNO_3 = \underset{\text{Cupric nitrate}}{3Cu(NO_3)_2} + 4H_2O + \underset{\text{Nitric oxide}}{2NO}$$

$$4Zn + 10HNO_3 = \underset{\text{Zinc nitrate}}{4Zn(NO_3)_2} + 5H_2O + \underset{\text{Nitrous oxide}}{N_2O}.$$

Nitric acid readily attacks organic matter such as sawdust and paper, and it acts on the human skin, turning it yellow. It is much used in the dyeing and explosive industries and in the manufacture of fertilisers.

Some common bases:

Quicklime, CaO (Calcium Oxide); and
Slaked Lime, $Ca(OH)_2$ (Calcium Hydroxide).

Manufacture.—When limestone or chalk or marble is heated strongly, carbon dioxide is given off and quicklime is left behind.

$$\underset{\text{Limestone}}{CaCO_3} = \underset{\substack{\text{Quick-}\\\text{lime}}}{CaO} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2}.$$

This is essentially the principle of the process of the burning of limestone to form lime, but as coal is often mixed with the limestone, the reaction is better indicated by the equation—

$$CaCO_3 + \underset{\substack{\text{Carbon of}\\\text{the coal}}}{C} = \underset{\substack{\text{Quick-}\\\text{lime}}}{CaO} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{2CO}.$$

When a little water is added to some freshly-made quicklime the mass becomes hot, steam is liberated, and a fine powder called slaked lime is obtained.

$$CaO + H_2O = \underset{\substack{\text{Slaked lime or}\\\text{calcium hydroxide}}}{Ca(OH)_2}.$$

Properties.—Slaked lime is only slightly soluble in water, and a milky mixture of lime and water is known as " milk of lime." When this is allowed to stand, the lime settles to the bottom, and the clear liquid on top is "lime-water." It has a characteristic taste and is alkaline to litmus—*i.e.*, turns red litmus blue. At ordinary temperatures 100 grams of water dissolve only 0·16 gram of calcium hydroxide or slaked lime.

When the gas carbon dioxide is bubbled through some clear lime-water, the clear solution is first turned milky, but on continuing to bubble the carbon dioxide through the milky solution the solution becomes clear again (see p. 160).

Lime neutralises acids forming salts and water.

Mortar is a paste formed by mixing sand with slaked lime and water. The setting of mortar is due to its loss of water and to its absorption of carbon dioxide from the air to form calcium carbonate, though this absorption appears to be very slow. The object of introducing sand is to render the mass more porous and at the same time to prevent an undue amount of shrinkage.

Lime is very important industrially. It is used in the preparation of mortars, in the manufacture of cements, glass, bleaching powder, and fertilisers. It is also used for drying certain gases, for removing carbon dioxide and sulphuretted hydrogen from coal gas, and in the treatment of hides before tanning. Lime as a fertiliser may be used either alone or combined with nitric acid, as calcium nitrate and the like (see p. 130). It is also employed for softening water (see p. 215). Hydraulic cements which set under water, such as **Portland cement,** consist essentially of the following:

Quicklime	(CaO)	about	65	per cent.
Silica	(SiO_2)	,,	21	,,
Alumina	(Al_2O_3)	,,	7	,,
Iron oxide	(Fe_2O_3)	,,	3	,,
Calcium sulphate	($CaSO_4$)	,,	2	,,
Magnesia	(MgO)	,,	1	,,
Water, carbon dioxide, etc.		,,	1	,,

The carbon dioxide is an impurity, and is combined with a little of the lime present to form calcium carbonate. The whole mixture is ground to a very fine powder. The setting of such cements is due to the formation of complex compounds, principally silicates of calcium and aluminium.

Caustic Soda, NaOH.

Also known as Sodium Hydroxide or Sodium Hydrate.

Manufacture.—An electric current is passed through brine—*i.e.*, through a solution of common salt (sodium chloride). Chlorine gas is given off at one pole or electrode, and metallic sodium is formed at the other. In the manufacture it is arranged that the pole at which the sodium is formed (the positive pole or *anode*) is composed of mercury, and the sodium immediately alloys with the mercury to form sodium amalgam. This amalgam flows into a separate vessel (as fast as it is formed), where it reacts with water yielding hydrogen, caustic soda solution, and mercury. The hydrogen is given off; the mercury is used again; and the caustic soda solution is heated until the water is driven off and the solid caustic soda obtained.

Electrolysis of brine may be indicated thus:*

$$NaCl = Na^+ + Cl^-.$$

The action of sodium amalgam on water is the same, chemically, as that of sodium alone:

$$2Na + 2H_2O = 2NaOH + H_2.$$

---

* The notation adopted in this equation is that usually employed for electrolytic reactions. The salt when in solution is supposed to be split up into two parts: the one a metal, the other an acid radicle. The metal portion is positively, and the acid radicle negatively, electrified. The passage of an electric current neutralises the various charges, and sets the individuals free to yield ordinary molecules of the various substances at the electrodes. When a salt is dissolved, it is always more or less separated into the above positively and negatively charged components. It is said to be *ionised*, and the components are referred to as positive *ions* (or *cations*) and negative *ions* (or *anions*). Ions are therefore electrically charged portions of molecules or radicles; they must not be confused with atoms or molecules, and the behaviour of a substance in the ionised form in solution is in many respects different from its behaviour in the ordinary molecular state. It should be further noted that the cation is not necessarily a metal; it may be a metallic radicle, such as NH_4^+ or H^+. The ionic hypothesis has proved most useful in explaining the various chemical actions which take place in solution.

Properties.—Caustic soda is a white crystalline hygroscopic solid. It rapidly absorbs carbon dioxide from the air, and is therefore used in breathing apparatus to absorb this gas from the exhaled breath. (For composition of exhaled air, see p. 166.)

$$2NaOH + CO_2 = \underset{\text{Sodium carbonate}}{Na_2CO_3} + H_2O.$$

Sodium carbonate, it is seen, is formed in the process, and this, with the moisture present, forms a cake or crust on the caustic soda and tends to prevent further absorption of the carbon dioxide. It is necessary, therefore, that a large surface of caustic soda be available, and the regenerator of the apparatus is usually constructed with this in view.

Caustic soda is a very strong base, readily neutralising acids to form salts and water. *E.g*:

$$NaOH + HCl = NaCl + H_2O.$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$
$$NaOH + HNO_3 = NaNO_3 + H_2O.$$

Caustic soda is very corrosive to many metals; it dissolves readily in water, giving off much heat, and its solution turns red litmus blue. Caustic soda melts easily, and is often cast into sticks for convenience in use. It is used industrially in the processes of bleaching, dyeing, refining of oils, and the making of soap.

Caustic Potash, KOH.

Also known as Potassium Hydroxide or Potassium Hydrate.

Manufacture.—Similar to that of caustic soda, a solution of potassium chloride (KCl) being electrolysed.

Properties.—Practically the same as those of caustic soda. Caustic potash is more expensive than caustic soda, and is therefore never employed where the latter is equally suitable. It is used in the manufacture of soft soap. Its reactions with acids are indicated in the following equations, a salt and water being formed in each case:

$$KOH + HCl = KCl + H_2O.$$
$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$
$$KOH + HNO_3 = KNO_3 + H_2O.$$

Ammonia, NH_3. Also known as Spirits of Hartshorn.

Ammonia is present in minute quantities in the air and in natural waters. It is produced by the action of bacteria on organic matter containing nitrogen, and is obtained generally when such organic matter " decays " or " rots." The smell of ammonia is common in stables (see p.138).

Manufacture.—Ammonia is obtained as a by-product in the distillation of coal at gas works or in coke-oven plants. Coal usually contains about 1 per cent. nitrogen, 6 to 20 per cent. of which goes to form the ammonia. Ammonia may be prepared in the laboratory by heating sal-ammoniac (ammonium chloride) with slaked lime. The ammonium chloride (NH_4Cl) and slaked lime ($Ca(OH)_2$) are mixed and introduced into a hard glass tube, and some quicklime is finally packed in towards the mouth of the tube to dry the gas as it is evolved.

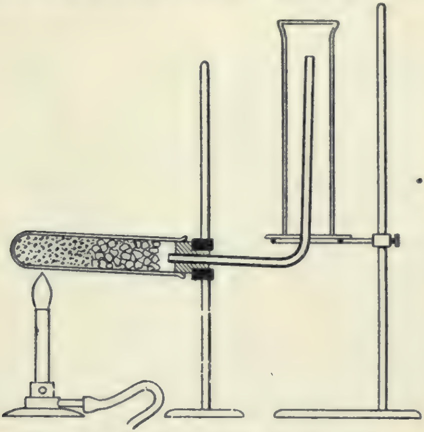


FIG. 71.—PREPARATION OF AMMONIA.

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O$$

Ammonia, being much lighter than air, can be collected, as shown in Fig. 71.

Properties.—Ammonia is a colourless gas with a most pungent smell. Its molecular weight is $(14 + 3 =)$ 17 and its density $(\frac{17}{2} =)$ 8·5. As the density of air is about 14·4, ammonia is a very light gas. It is very soluble in water, 1 volume of water at 0° C. dissolving about 1,150 volumes of ammonia. Its solution is alkaline to litmus, and is commonly regarded as NH_4OH, ammonium hydroxide, though the aqueous solution appears also to contain free ammonia, NH_3.

Ammonium hydroxide neutralises acids to form salts and water, the radicle NH_4 behaving as a metal. *E.g.:*

$$NH_4OH + HCl = \underset{\text{Ammonium chloride}}{NH_4Cl} + H_2O.$$

$$2NH_4OH + H_2SO_4 = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + 2H_2O.$$

$$NH_4OH + HNO_3 = \underset{\text{Ammonium nitrate}}{NH_4NO_3} + H_2O.$$

Ammonia is easily liquefied, and the low temperature obtainable on the evaporation of the liquid is made use of in various ways, such as in refrigerators and in the freezing system of sinking shafts through water-bearing strata. Carbon dioxide when liquefied is also used for similar purposes, but leakage is more easily detected in the case of ammonia, due to its strong smell. (Carbon dioxide is odourless.) Ammonia does not burn in air unless the ammonia has been preheated. This may be done by passing it through a strongly heated tube before it emerges to the atmosphere. It may then be lit at a jet, when it burns with a greenish-yellow flame.

Ammonia burns in oxygen to form nitrogen and water:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

The presence of ammonia in water supplies is regarded as evidence of pollution by sewage or the like. A delicate test for such ammonia is afforded by Nessler's solution, which, in the presence of a trace of ammonia, yields a brown precipitate. Nessler's solution consists of mercuric iodide + potassium iodide (a double iodide) dissolved in caustic potash solution. The reaction with ammonium chloride is indicated in the equation—

$$NH_4Cl + \underset{\text{Mercuric potassium iodide}}{2(HgI_2.2KI)} + 4KOH$$

$$= \underset{\text{Brown precipitate}}{NHg_2I.H_2O} + \underset{\substack{\text{Potassium}\\\text{iodide}}}{7KI} + \underset{\substack{\text{Potassium}\\\text{chloride}}}{KCl} + 3H_2O.$$

CHAPTER X

SOME COMMON SUBSTANCES—MAINLY SALTS.

Common Salt, NaCl.

Also known as Sodium Chloride or as Salt.

Common salt occurs very widely distributed. Sea water contains about 2·5 per cent. of it, and it is the essential constituent of rock-salt deposits. Salt is found principally in strata of Triassic or Permian Age in England, and these frequently overlie the coal measures. Rock salt is mined considerably in Cheshire at Nantwich and Northwich. It is now obtained largely by pumping water down boreholes into the salt-bearing strata, allowing the water to dissolve some of the salt, pumping back the brine to the surface, and evaporating off the water in shallow iron pans to leave the salt behind as a residue.

It is interesting to note that salt water is often found along with petroleum deposits.

Salt may be made in the laboratory by neutralising caustic soda solution with hydrochloric acid and evaporating off the water:

$$NaOH + HCl = NaCl + H_2O.$$

Properties.—Common salt is a white crystalline solid not very soluble in water. It crystallises in cubes. It has a characteristic taste—saline. The commercial salt often tends to "cake," due to the presence of a small amount of the chlorides of calcium and magnesium which are hygroscopic and so take up moisture from the atmosphere. Salt is necessary for animal food. In the gastric juices of the stomach there is about 0·1 per cent. hydrochloric acid present which is derived from the salt taken in by an action denoted by the equation—

$$NaCl + H_2O = NaOH + HCl.$$

This is the reverse of the common laboratory reaction. From salt are obtained the following: Hydrochloric acid, sodium carbonate, sodium bicarbonate, sodium sulphate, sodium thiosulphate (*i.e.*, the "hypo" of photography), chlorine gas, bleaching powder, etc.

Sodium Nitrate, $NaNO_3$.

Also known as Chile Saltpetre or as Caliche.

It is found in large quantities in Chile.

In the laboratory it can be made by neutralising a solution of caustic soda with nitric acid and evaporating off the water:

$$NaOH + HNO_3 = NaNO_3 + H_2O.$$

Properties.—Sodium nitrate is a white hygroscopic salt readily soluble in water. Though cheaper than potassium nitrate, it is *not* used in gunpowder (see p. 220) in place of potassium nitrate because of its hygroscopic nature. When sodium nitrate is heated strongly, oxygen, nitrogen, and oxides of nitrogen are evolved. It is used in the manufacture of nitric and sulphuric acids, and also as a manure (artificial). In some explosives where special precautions are taken to exclude moisture, sodium nitrate is employed.

Potassium Nitrate, KNO_3.

Also known as Saltpetre or as Nitre. It is found as an incrustation on the soils of hot *arid* countries such as India, Persia, and Arabia. Its origin is thought to be due to the action of bacteria on organic matter containing nitrogen. The nitrogen is first converted into ammonia and ammonium compounds, and these are then changed by certain bacteria into nitrous acid, HNO_2, which in turn is converted by certain other bacteria into nitric acid, HNO_3. The nitric acid finally attacks any potash (K_2CO_3), always present in vegetable life and remains, and yields potassium nitrate.

In the laboratory, nitre can be prepared by neutralising a solution of caustic potash with nitric acid and evaporating off the water:

$$KOH + HNO_3 = KNO_3 + H_2O.$$

Properties.—Potassium nitrate or nitre is a white crystalline substance and is *not* hygroscopic. It is easily soluble in water, particularly in hot water. Nitre melts at 339° C., and on heating further it gives off oxygen and forms potassium nitrite—

$$2KNO_3 = 2KNO_2 + O_2.$$

It is used principally in the manufacture of gunpowder (see p. 220), where its function is to supply the oxygen for the rapid combustion of the charcoal and sulphur.

Sodium Carbonate, Na_2CO_3.

Also known as Soda-ash or as Mild Marine Alkali. It can be obtained from the water-soluble part of the ashes of sea plants, but it is manufactured by the following processes:

Leblanc Process.—Common salt is heated with strong sulphuric acid, which converts the salt to sodium sulphate. Hydrochloric acid fumes are evolved:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The sodium sulphate, or "salt-cake," as it is called, is then heated with fine coal and chalk in a furnace when the following action takes place:

$$Na_2SO_4 + \underset{\substack{\text{Carbon of}\\\text{the coal}}}{4C} + \underset{\text{Chalk}}{CaCO_3} = Na_2CO_3 + \underset{\substack{\text{Calcium}\\\text{sulphide}}}{CaS} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{4CO}.$$

Carbon monoxide is given off, and the residue of sodium carbonate and calcium sulphide, known as "black ash," is treated with cold water, which dissolves all the sodium carbonate but very little calcium sulphide. On evaporating this solution to dryness, impure sodium carbonate, called "soda-ash," is obtained. If the solution is evaporated only until crystals begin to form, and these crystals are then allowed to "grow" and separate out of their own accord, the substance formed is "washing soda," $Na_2CO_3.10H_2O$.

Note.—The hydrochloric acid fumes given off in the first instance are absorbed in water to yield muriatic acid as a valuable by-product.

Solvay Ammonia-Soda Process.—Carbon dioxide is bubbled through a brine solution saturated with ammonia. Sodium bicarbonate is precipitated, being much less soluble than the ammonium chloride formed:

$$NaCl + NH_4OH + CO_2 = \underset{\substack{\text{Sodium} \\ \text{bicarbonate}}}{NaHCO_3} + \underset{\substack{\text{Ammonium} \\ \text{chloride}}}{NH_4Cl}.$$

To obtain sodium carbonate from the bicarbonate it is only necessary to heat the latter:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The CO_2 (carbon dioxide) evolved is used over again for the first reaction. Moreover, the ammonia required for saturating the brine is easily obtained from the ammonium chloride by heating the latter with lime, CaO:

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

The lime is obtained by strongly heating limestone, which is also an additional source of CO_2:

$$CaCO_3 = CaO + CO_2.$$

The whole of the operations are therefore practically a cycle—an object studiously to be striven after in such manufacturing work.

Properties.—Sodium carbonate as soda-ash is a white powder with a characteristic bitter taste and strong alkaline reaction. It neutralises acids, forming carbon dioxide and the sodium salt of the acid:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

Sodium carbonate as washing soda contains ten molecules of water of crystallisation, and therefore has the formula $Na_2CO_3.10H_2O$. On heating washing soda the water is driven off, leaving Na_2CO_3. In air crystals of washing soda effloresce or crumble to a white powder, having the composition $Na_2CO_3.H_2O$.

Sodium carbonate is used for softening water (see p. 215);

as a flux in the reduction of metals from their ores; in glass manufacture; and as a mild alkali in the chemical industries in general.

Potassium Carbonate, K_2CO_3.

Also known as Potash and Mild Vegetable Alkali. It may be obtained from the water-soluble part of the ashes of land plants by evaporating the solution, but it is generally manufactured from *potassium* sulphate by the Leblanc Process (see p. 139).

Its properties and uses are similar to those of sodium carbonate, but it is more expensive and therefore seldom employed where soda-ash is equally serviceable. It is used, however, in the manufacture of certain types of glass.

Calcium Carbonate, $CaCO_3$.

Occurs as the essential constituent of chalk, limestone, marble, coral, and Iceland spar. It is found in nature in enormous quantities, principally in rocks formed by the accumulation of shells and tests of marine organisms.

Properties.—Chalk and limestone are used for the manufacture of lime for cements and mortar (see p. 132); for bleaching powder ($CaOCl_2$); for artificial manures, such as calcium nitrate, $Ca(NO_3)_2$; and as a source of carbon dioxide.

Limestones are frequently excellent building stones, and the use of marble as an ornamental stone is well known. The magnesian limestone of Permian Age is not a very good weathering stone, though suitable for carving. The Houses of Parliament are built of this stone. The limestones of Jurassic Age provide the best building limestones—*e.g.*, the famous Portland Stone.

Ammonium Chloride, NH_4Cl.

Also known as Sal-ammoniac.

Ammonium chloride may be obtained by passing ammonia, obtained from the ammonia liquor of gas works or coke-ovens, into hydrochloric acid solution:

$$NH_3 + HCl = NH_4Cl.$$

Properties.—Ammonium chloride is a white crystalline solid, easily volatilised by heating, the vapour of the ammonium chloride breaking up or "dissociating" into ammonia and hydrochloric acid. A cloud of ammonium chloride, however, is produced when ammonia (gas) and hydrochloric acid (gas) are brought into contact at ordinary temperatures.

Ammonium chloride or sal-ammoniac is largely used in Leclanché electric cells, in both the wet and dry types.

Ammonium Nitrate, NH_4NO_3.

Ammonium nitrate is obtained by neutralising ammonia solution with nitric acid and evaporating to crystallising-point:

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$

Properties.—Ammonium nitrate is a white crystalline substance, somewhat deliquescent. On heating it yields nitrous oxide (N_2O), also known as laughing-gas, and employed by the dentist as an anæsthetic:

$$NH_4NO_3 = N_2O + 2H_2O.$$

Heated strongly it is liable to explode.

It is used largely in certain types of explosive (see p. 228) along with other compounds; with ice and water ammonium nitrate forms an excellent freezing mixture. When used in explosives precautions have to be taken to ensure that the cartridge case is waterproof owing to the hygroscopic (deliquescent) nature of ammonium nitrate.

Ammonium Sulphate, $(NH_4)_2SO_4$.

Ammonium sulphate is obtained by neutralising dilute sulphuric acid with ammonia solution and evaporating:

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O.$$

It is commonly manufactured at gas works or coke-oven plant by passing the ammonia (distilled from the ammonia liquor) into dilute sulphuric acid.

Properties.—Ammonium sulphate is a most valuable artificial manure. It should not, however, be used along with lime as a manure, as this will result in the formation of calcium sulphate and free ammonia, which is harmful:

$$(NH_4)_2SO_4 + CaO = CaSO_4 + 2NH_3 + H_2O.$$

This reaction is often made use of to obtain ammonia for the manufacture of other ammonium salts from the ammonium sulphate of the gas works.

Iron Pyrites, FeS_2.

Also known as Iron Disulphide or as "Brasses." Iron pyrites is found associated with most coal seams. It is generally in the form of balls or nodules, but it is sometimes present as fine grains. There are two principal varieties of pyrites: one crystallises in the cubic system (in cubes, etc.); the other crystallises in the rhombic system (*i.e.*, in crystals whose three axes are at right angles but unequal). The rhombic or marcasite pyrites weathers in the mine more readily to sulphuric acid, etc., than the cubic variety. In the process of weathering (principally oxidation) the marcasite pyrites swells and tends to break up the coal in which it is encased. At the same time a small amount of heat is developed due to the oxidation, and the coal is reduced to a form in which it is rather liable to spontaneous combustion (see p. 174). This has been suggested as accounting for the origin of certain spontaneous outbreaks of heating in coal; and it is possible that where the marcasite is more or less disseminated it may have some small influence in promoting such combustion, but whether this influence is appreciable is now doubted.

Iron pyrites is used in the manufacture of sulphuric acid, and the residue of iron oxide left in the operation is sometimes used for making cast iron or for absorbing the sulphuretted hydrogen from coal gas.

Sulphur, S. Atomic lot = 32.

Sulphur is obtained native as brimstone in volcanic districts, such as Sicily. It is purified by stacking it on a sloping floor and setting fire to the sulphur at the bottom.

About one-quarter of the sulphur burns away and the heat melts the remainder and causes it to run. It is led into prepared channels or moulds (Figs. 72 and 73). It is finally purified by distillation, the condensed fumes being known as flowers of sulphur if the distillation is carried out slowly, or roll sulphur if the distillation is rapid.

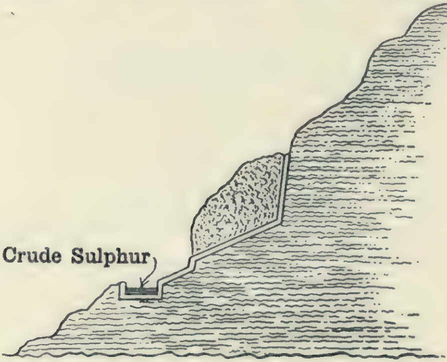


FIG. 72.—EXTRACTION OF SULPHUR.

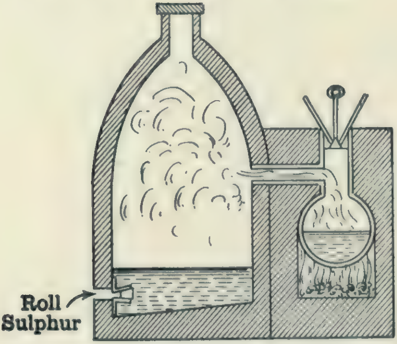


FIG. 73.—PURIFICATION OF SULPHUR.

Properties.—Sulphur is an element which burns in air to give sulphur dioxide, SO_2, a poisonous suffocating gas:

$$S + O_2 = SO_2.$$

Sulphur melts at 114° C. and boils at 448° C. Many of the most important metallic ores are combinations of the metals with sulphur and are known as sulphides. *E.g.*—

Ore.	*Formula.*
Galena or lead sulphide	PbS.
Blende or zinc sulphide	ZnS.
Cinnabar or mercury sulphide	HgS.
Pyrites or iron disulphide	FeS_2.
Chalcopyrite or iron pyrites	$CuFeS_2$.
Mispickel or arsenical pyrites	$FeAsS$.
Stibnite or antimony sulphide	Sb_2S_3.

Carbon, C. Atomic weight = 12.

Carbon occurs free in a variety of forms in nature, the purest being the diamond. It also occurs as graphite, as charcoal, as soot, as coke, etc., but in each of these cases it is usually contaminated with more or less of impurity. The bulk of the carbon present in coal is thought to be chemically combined with other elements, though in certain coals such as anthracites free carbon may be present in large amount.

Diamonds, when burnt in oxygen, yield carbon dioxide and nothing else. *Graphite* often contains much mineral matter mixed with its carbon. Graphite is used as a lubricant and also in the manufacture of ordinary lead pencils.

Charcoal, soot, coke, etc., are still less pure forms of carbon.

Chemically combined carbon is found throughout the vegetable and animal world in all organic substances; also in carbon dioxide gas and in carbonates; in mineral and vegetable oils, and all varieties of coal.

Dried wood contains about 50 per cent. of carbon; ordinary bituminous coal contains 80 to 90 per cent. of carbon.

Properties.—Carbon, except the diamond variety, is a good conductor of heat and electricity. It is a non-metal, like sulphur, phosphorus, etc., but it is unlike most non-metals in its good conductivity of heat and electricity.

Carbon has a valency of 4. The various combinations of carbon with hydrogen and often oxygen give rise to an enormous number of compounds, known as organic. Nitrogen and sulphur and a few other elements also combine with the carbon, etc., of the above organic compounds, yielding still more numerous bodies.

Sand, Quartz, and Silica.

Sand consists essentially of small grains of quartz frequently coloured yellow or brown with a little iron oxide. Quartz is a chemical compound, silicon dioxide, SiO_2, or silica; and it is the common form in which free silica occurs. When pure it is a colourless crystalline substance of specific gravity 2·6 and hard enough to cut glass. Sands are formed by the denudation or wearing down of igneous or sedimentary rocks containing quartz. Sandstones are sands which have been compressed in the course of ages in the earth's crust and the sand grains have become more or less cemented together, yielding a solid rock. There is also an amorphous variety of silica, called opal silica, in which there is from 3 to 12 per cent. of water present. Such silica has generally been formed from silicates by weathering processes.

The vast majority of the rocks of the earth's crust contain large quantities of either free silica or silica combined with such bases as potash, soda, lime, or alumina to yield silicates.

Properties.—Quartz is not attacked by acids except hydrofluoric acid, HF. It will withstand very high temperatures (up to 1,600° C.) without melting, and silica bricks are often employed as a refractory material for lining furnaces, for coke-oven walls, etc. Silica (as sand) is used in mixing mortar, in making silica bricks, and in the manufacture of glass. Silica as kieselguhr is employed in dynamite to absorb the nitro-glycerine.

The physiological effects of silica dust in the mine air are important. Fine quartz grains have an injurious effect on the lungs if inhaled in any quantity, and it is advisable to use a supply of water when drilling through siliceous rock. Fortunately, drilling through such ground is not so common in coal-mining as in metalliferous mining, so that coal-miners are by no means subject to diseases of the lungs to the same extent as are metal-miners. On account of this objectionable property of fine silica particles suspended in the air, a rock containing much free silica (quartz) should not be used for grinding to powder form for " stone-dusting " purposes.

Silicates and Clays.—Silicates are chemical compounds of silica and some base or bases such as lime or alumina.

Some of the commonest silicates are:

Silicate.	*Chemical Formula.*
Felspar (potash or orthoclase felspar)	$K_2O.Al_2O_3.6SiO_2$—*i.e.*, potassium aluminium silicate.
Felspar (soda felspar) . .	$Na_2O.Al_2O_3.6SiO_2$—*i.e.*, sodium aluminium silicate.
Anorthite (lime felspar)	$CaO.Al_2O_3.2SiO_2$—*i.e.*, calcium aluminium silicate.
Kaolin (china clay) . .	$Al_2O_3.2SiO_2.2H_2O$—*i.e.*, aluminium silicate (hydrated).

Kaolin.—Kaolin is formed from the weathering of felspars, which are among the chief constituents of such igneous rocks as granites. Clays consist essentially of kaolin, but frequently they contain large quantities of other substances.

Fireclays as a rule contain 50 to 60 per cent. silica, 20 to 30 per cent. alumina, about 3 per cent. iron oxide, 1 per cent. of lime, 0·4 to 1 per cent. of potash and soda, and 8 to 14 per cent. of combined water and organic matter.

Gannister is often classed as a fireclay containing a large excess of silica, but it is almost a sandstone. It consists of over 95 per cent. of silica with small quantities of alumina, lime, iron oxide, and magnesia. It usually occurs in the Lower Coal Measures, and is useful for making into refractory bricks to withstand high temperatures.

Shales.—Shales are also silicates of aluminium and are essentially compressed clays. In a shale the bedding places are usually well developed, so that it easily cleaves into layers. If the shale becomes highly compressed in the earth's crust, fresh cleavage planes are formed, often nearly at right angles to the original bedding planes. A shale so altered (metamorphosed) becomes a **slate.**

An **oil shale** is a shale impregnated with a certain quantity of organic matter called kerogen. On distilling these shales, oils are obtained resembling those found in petroleum (see p. 189). The yield of oil varies from 10 to 40 gallons per ton of shale. The industry flourishes in the Lothians of Scotland and is also commencing in Norfolk. In Scotland the oil shales occur in the Calciferous Sandstone Series at the base of the Carboniferous Formation, whereas in Norfolk (and Dorset) the oil shales occur in the Kimmeridge Clays in the Upper Oolites of Jurassic Age. In addition to oils there are also obtained, on distilling oil shales, considerable quantities of paraffin wax, ammonium sulphate, and gas, the gas being used for heating the retorts, as in coke-oven practice (see p. 189).

CHAPTER XI

THE ATMOSPHERE.

AIR consists essentially of a mixture of two gases—oxygen and nitrogen—though various other gases are always present. Dry air has the following average percentage composition:

	By Weight.	*By Volume.*
Nitrogen	75·51	78·03
Oxygen	23·15	21·00
Argon, etc.	1·30	0·94
Carbon dioxide	0·04	0·03

There is a very variable quantity of water vapour present (see p. 75), averaging 1 per cent., and minute traces of ammonia, nitric acid, and sulphuric acid have been shown to be present.

Nitrogen and Argon.

Nitrogen, N.

Atomic weight = 14; molecular weight = 28; density = 14; specific gravity $\frac{14}{14 \cdot 4} = 0 \cdot 972$.

Occurrence.—Nitrogen occurs very widely distributed both in the free state in the atmosphere and combined in animal and vegetable matter, in nitrates and in ammonia, and ammonium compounds.

Preparation.—Pass air over a heated metal—*e.g.*, copper turnings. The copper combines with the oxygen to form copper oxide, and the residual gas, mainly nitrogen, passes on and may be collected over water (see p. 97, Fig. 59).

Properties.—Nitrogen is a colourless, odourless, tasteless gas, practically insoluble in water. It neither burns nor supports combustion. It will not support life, but is clearly not poisonous. It is essential for plant and animal growth. Free nitrogen (*i.e.*, nitrogen in the molecular form as in air) is chemically very inactive and will not combine directly with most bodies. Combined nitrogen, however (*i.e.*, nitrogen in the atomic form), is exceptionally active, and its activity is seen in such bodies as nitroglycerine, ammonium nitrate, and practically all explosives. Nitrogen is a constituent of black-damp and afterdamp (see p. 176).

Argon

Is a colourless, odourless, tasteless gas, very much like (free) nitrogen in its inactivity, and is usually considered along with nitrogen (almost *as* nitrogen) in forming the inactive or passive part of the atmosphere in contrast to the oxygen, the active portion. There are also minute traces of other similarly inert gases in the atmosphere such as helium, neon, krypton, and xenon, but these interest only the chemical specialist. It is interesting to note that argon, unlike oxygen, hydrogen, and nitrogen, appears to contain only 1 atom per molecule. Its atomic weight and molecular weight are therefore equal—viz., 40.

Analysis of Air.

Gas analyses are usually expressed in percentages by volume of the various constituents. As there is only about 0·03 per cent. of carbon dioxide in the atmosphere, the accurate estimation of the amount of this gas present in a sample of air demands apparatus graduated to read very small changes in volume if ordinary absorption methods are adopted. In the case of oxygen, however, as there is approximately one-fifth of the gas present in air, the estimation to within a reasonable degree of accuracy may be done without such finely graduated apparatus. Oxygen is absorbed by a solution of pyrogallic acid in caustic potash. This solution, it should be noted, absorbs also any carbon dioxide, due to the presence of the caustic potash, so that if an accurate estimation of the oxygen is required the air should first be deprived of its carbon dioxide by passing it into a solution of caustic potash alone.

A convenient type of apparatus for the oxygen determination is **Hempel's** (Fig. 74).

The apparatus consists of:

1. Two burettes *R* and *G*, *G* being graduated, connected together at the base by 2 to 3 feet of rubber tubing, *D*. Burette *G* is fitted with two taps, *T* and T_2.

2. An absorption gas pipette consisting of two bulbs *B* and *C*, which are in connection *via* a piece of fairly wide tubing, as shown. The piece of tubing, *A*, leading from bulb *B* is of fine bore, however, as is also the connecting-piece *K*.

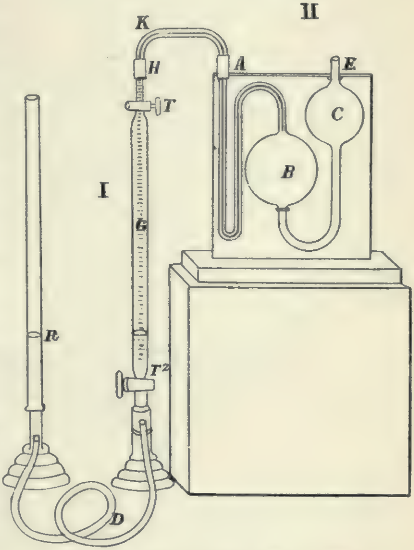


FIG. 74.—HEMPEL'S APPARATUS.

The burettes and pipette are first disconnected at *H*. To make up the alkaline pyrogallic acid solution dissolve about 80 grams of caustic potash in 100 c.c. of water and add 10 grams of pyrogallic acid. Shake up in a stoppered vessel in order to exclude air as far as possible. This solution is now drawn into *B* through *K*, until there is rather more than sufficient to fill bulb *B* completely. *A* and *E* are then closed—*A* with a clip and *E* with a cork—to prevent access of air. The burettes are taken, and water is poured down *R* until *R* and *G* are about half full, taps *T* and T_2 being open. Next expel the air from *G* by raising *R*, and introduce the sample of air *via* *H* into *G* by lowering *R*. About 100 c.c. of air may be taken. Now close tap *T*, bring the water surfaces in *R* and *G* to the same level, and read the volume of air in *G*. This reading gives the volume at atmospheric pressure of the air to be analysed. The pipette is next connected up at *H*, the tubes *A* and *K* being first filled with the alkaline pyrogallic acid solution by blowing gently at *E*. The clip at *A* is removed. In order now to pass the gas over into bulb *B* where the oxygen will be absorbed, *R* is raised, tap *T* opened, and the cork removed from *E*. When the water from *G* has risen into the tube *K*, *T* is closed.

The absorption of the gas requires some few minutes, and during this time the absorption may be assisted by shaking the pipette. After five minutes, tap *T* is opened and *R* is lowered until tubes *A* and *K* are full of the absorbent, as before. Tap *T* is then closed, the pressure brought to atmospheric by levelling the water surfaces in *R* and *G*, and the volume of gas in *G* is read. This gas is then again passed over the absorbent in the pipette for a few minutes and taken back into *G* and the volume in *G* at atmospheric pressure noted. The procedure is continued until a constant reading is obtained—*i.e.*, until all the oxygen (and CO_2) have been absorbed.

Initial reading of *G* = 99·8 c.c.
Reading of *G* after one absorption = 80·1 ,,
,, ,, ,, second ,, = 78·9 ,,
,, ,, ,, third ,, = 78·9 ,,

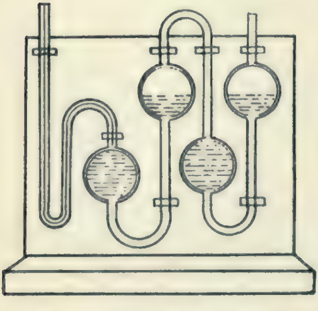


Fig. 75.—Hempel Pipette.

$$\therefore \text{ Absorption} = 99\cdot 8 - 78\cdot 9 = 20\cdot 9 \text{ c.c.}$$

$\therefore$ Percentage (oxygen + CO_2) is $\frac{20\cdot 9}{99\cdot 8} \times 100 = \mathbf{20\cdot 92}$.

Note.—In some forms of pipette (Fig. 75) four bulbs are used instead of two, the additional two bulbs being filled with water or other liquid to protect the absorbent from the outside air. Pyrogallic acid solution is best kept in a four-bulb pipette of this type.

The **Haldane Gas Analysis Apparatus** (Fig. 76), commonly used for mine-air analysis, consists essentially of (1) a finely graduated burette, *B*, in place of the more or less roughly graduated burette, *G*, used in the Hempel apparatus; (2) a pipette, *C*, containing caustic potash solution for absorbing carbon dioxide; (3) a pipette, *T*, called the combustion pipette, containing a fine piece of (insulated) platinum wire over mercury for estimating the amount of inflammable gas; (4) a pipette, O, containing alkaline pyrogallic acid solution for absorbing oxygen. The various pipettes may each be connected to the burette by taps and fine-bore glass tubing. In place of water in the burette, *B*, and tube, *L*, mercury is used, as some gases are more soluble in water than are others. In principle, therefore, the Haldane apparatus is a compact form of Hempel apparatus. The use of the combustion pipette in burning any inflammable gas in the air sample is important. The ends of the platinum wire are connected to a 4-volt accumulator (not shown), which heats the platinum to a bright heat. In the presence of such glowing platinum, any inflammable gas is rapidly burnt (see p. 189). In measuring the volume of a gas the slightest change in temperature or pressure may make appreciable differences. Such changes are reduced to a minimum or are corrected for by the following special contrivances:

(1) *N*, a similar burette to *B*, and called a control tube; (2) *J*, a glass jacket filled with water in which both burette, *B*, and control tube, *N*, are immersed, in order to keep the temperatures of the burette and control tube constant, or nearly so.

For exact details of the use of the apparatus the reader is referred to *Methods of Air Analysis*, by J. S. S. Haldane (Chas. Griffin, publishers). The main principles, however, are as follows:

The gas sample is taken into burette *B* via *Z*—over mercury—and the volume read on *B* after opening tap *D* to the potash and adjusting the latter to mark *W*. The sample is then driven over into the pipette *C* by raising *L*, the taps being properly set. In *C* the caustic potash solution absorbs any CO_2. After

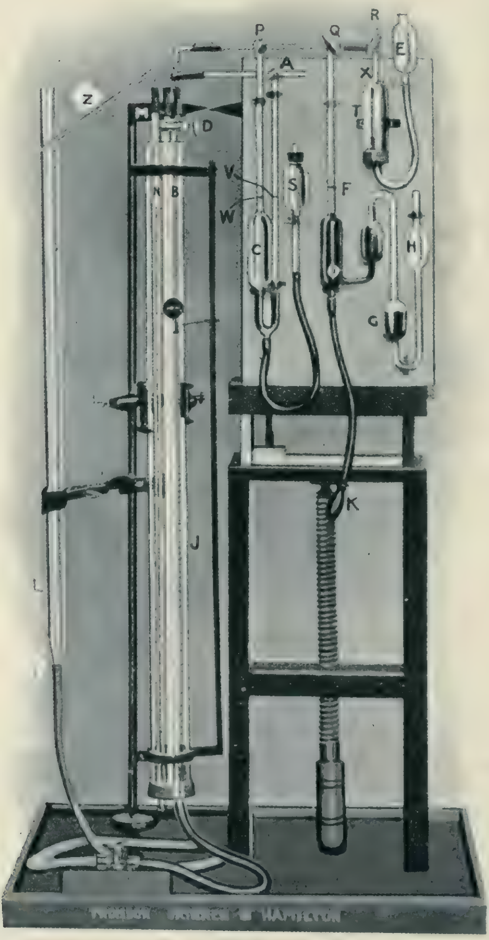


FIG. 76.—HALDANE'S APPARATUS.

a few minutes the gas is drawn back into *B* by lowering *L*, and any decrease in volume noted. This decrease gives the volume of the CO_2 which was present. The gas is next driven over into *T*, where any combustible gas, such as methane, is burnt to CO_2 and H_2O by means of the glowing platinum wire. The amount of methane is obtained by then passing the gas back into *B*, noting the contraction in volume, passing the gas into the potash pipette *C* for a few minutes (to absorb the CO_2), again returning it to *B*, and noting any further decrease in volume. If methane is present, the amount of contraction after explosion should be twice the decrease in volume after passing over caustic potash solution—*i.e.*, twice the volume of carbon dioxide formed by combustion (see p. 189). Also, the volume of carbon dioxide thus formed is equal to the volume of the methane originally present. Finally, the gas is passed into the pyrogallic acid pipette, *O*, where the oxygen is absorbed, the absorption taking some ten to fifteen minutes. The residual gas is nitrogen, and it is used to "wash out" all the tubes which connect the various pipettes with *B*. This is done by manipulating the various taps and raising and lowering *L*. The washings are then passed into *O* to extract the small amount of oxygen which they contain. The decrease in volume is obtained as before by returning the gas to the graduated burette, *B*. This decrease, however, does not represent the whole of the oxygen present as part has been used up in burning the methane in *T*. The total amount of oxygen equals (the amount absorbed by the pyrogallic acid solution + an amount equal to twice the volume of the methane).

The apparatus is now ready for the next analysis, the inert gas nitrogen being in the short lengths of fine-bore tubing which connect the pipettes to burette *B*. The remaining nitrogen in *B* is driven out through *Z* by raising *L*, tap *D* being properly set.

Note.—1. Throughout the analysis the various liquids in the pipettes are always brought to their respective marks, *X* or *F* or *W*, before reading the volume on burette *B*.

2. In order to ensure that the absorption is complete, the gas is always returned to the same pipette, until a constant reading is obtained on *B*.

Oxygen, O.

Atomic weight = 16; molecular weight = 32; density = 16; specific gravity = 1·1.

Occurrence.—Free oxygen forms about one-fifth of the atmosphere by volume. In chemical combination oxygen is computed to constitute about one-half by weight of the earth's crust. It will be remembered that oxygen constitutes $\frac{8}{9}$ by weight of water. It is the most widely and lavishly distributed element.

Preparation.—1. Heat oxygen mixture and collect the gas given off over water (see Fig. 47). Oxygen mixture consists of about 3 parts by weight of potassium chlorate with 1 part by weight of manganese dioxide. The manganese dioxide assists in the liberation of oxygen without having undergone any change itself at the end of the experiment. Such "assisters" of reactions are known as "catalysts." The equation denoting the change may be written—

$$\underset{\substack{\text{Potassium}\\\text{chlorate}}}{2KClO_3} = \underset{\substack{\text{Potassium}\\\text{chloride}}}{2KCl} + 3O_2.$$

[Observe that chemical compounds containing much oxygen have their chemical names terminating in "-ate." Such are the sulph*ates* (SO_4), the carbon*ates* (CO_3), the nitr*ates* (NO_3), the chlor*ates* (ClO_3). Chemical compounds, however, containing only two substances have their names ending in "-ide," even though one of the substances be oxygen—*e.g.*, copper oxide, CuO; barium peroxide, BaO_2; sodium chloride, $NaCl$; iron disulphide, FeS_2; sodium peroxide, Na_2O_2; antimony sulphide, Sb_2S_3. The hydroxide (or hydrate) group, OH, is, of course, an exception to the above rule.]

2. Oxygen may also be obtained by heating such oxides as mercuric oxide (HgO), or red lead (Pb_3O_4), or barium peroxide (BaO_2).

Manufacture.—Oxygen is manufactured on the large scale from liquid air. The principle of the process lies in the fact that if liquid air be allowed to evaporate, the nitrogen evaporates more rapidly than does the oxygen, so that the gas escaping after evaporation has continued for a while is practically pure oxygen.

Properties.—Oxygen is a colourless, odourless, tasteless gas, slightly soluble in water, sufficiently so to enable fishes to breathe. It is necessary for animal life and for ordinary combustion. Oxygen does not burn of itself in air, but substances burn in oxygen much more brightly than they do in ordinary air. A piece of wood heated so as to glow dimly in air bursts into flame when introduced into a jar of oxygen. Phosphorus (P), sulphur (S), and carbon (C) (in the form of charcoal), burn brilliantly in the gas forming oxides—P_2O_5, SO_2 and SO_3, and CO_2. These oxides are soluble in water and their solutions are acidic. Sodium, magnesium, and many other metals burn in the gas to form oxides, which are basic (see p. 126). Perfectly dry oxygen is very inert and will not support combustion at all, but a trace of moisture is sufficient to cause the above vigorous chemical actions.

It is the oxygen of the air which is responsible for most of the chemical changes which take place in air, such as combustion, the rusting of iron, the rotting of timber, respiration, explosions of firedamp and coal dust, and the like. These phenomena are all included under the term **"oxidation,"** which signifies combination with oxygen. "Oxidation," however, is, in general, used to express: (1) Combination with oxygen; or (2) increase in the proportion of the non-metallic constituents of a compound; or (3) decrease in the proportion of hydrogen in a compound.

Examples of oxidation:

1. $C + O_2 = \underset{\text{Carbon dioxide}}{CO_2}$
2. $\underset{\text{Ferrous chloride}}{2FeCl_2} + Cl_2 = \underset{\text{Ferric chloride}}{2FeCl_3}.$
3. $\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + O_2 = \underset{\text{Acetaldehyde}}{2CH_3.CHO} + 2H_2O.$

In the last case (3) ethyl alcohol is oxidised to acetaldehyde by the loss of hydrogen.

Oxygen is used in breathing apparatus for rescue work. In such cases it is contained in strong iron cylinders under pressure. According to recent regulations of the Coal Mines Act, 1911, dated July 30, 1920, the oxygen in every cylinder shall be analysed before being used, and if the oxygen is found to contain more than 2 per cent. of impurities it shall not be used in any work or practice below ground, or in any practice above ground where the person wearing the apparatus is liable to be out of sight of the instructor. A record of the results of every analysis shall be kept. It is also laid down in the same regulations that the reducing valve for the oxygen delivery shall be so adjusted as to supply not less than two litres of oxygen per minute to the wearer. The function of oxygen in respiration and combustion generally is discussed in Chapter XII. In air analyses the oxygen is usually absorbed by an alkaline solution of pyrogallic acid (see p. 151). Mine air must contain not less than 19 per cent. oxygen in any working place.

Carbon Dioxide, CO_2.

Molecular weight = 44; density = 22; specific gravity = 1·5. Also known as Carbonic Acid Gas.

Occurrence.—Carbon dioxide is present in the free state to the extent of about 0·03 per cent. in air. It occurs combined in all carbonates of which the most plentiful is calcium carbonate, $CaCO_3$. $CaCO_3$ is the principal and sometimes the only constituent of limestone, chalk, and marble. Carbon dioxide is formed by the burning of any matter containing carbon, such as coal, wood, coke, oil, and so forth; also by the burning of limestone (p. 131), and by the breathing of men and animals.

In ordinary respiration only a small part of the oxygen inhaled is converted into carbon dioxide, a deep breath as a rule containing about 4 per cent. carbon dioxide (see p. 165). Other sources of carbon dioxide are: Fermentation—brewing—baking, "rotting" of timber, oxidation or decay of organic matter, animal or vegetable, action of acids on carbonates, and so forth. The reason that the carbon dioxide percentage in the atmosphere does not increase is partly owing to the fact that the gas is somewhat soluble in water (rain and sea water contain a fair amount), but mainly because the green colouring matter (chlorophyll) of plants absorbs carbon dioxide in sunlight, the carbon being retained by the plant for building up its structure and the oxygen being returned to the air.

Preparation.—1. By the action of an acid on a carbonate. Dilute hydrochloric acid and calcium carbonate in the form of limestone or marble are convenient. The apparatus is the same as that employed for the preparation of hydrogen (p. 119, Fig. 66), marble being, of course, substituted for the zinc, and hydrochloric acid for sulphuric acid—

$$CaCO_3 + 2HCl = \underset{\text{Calcium chloride}}{CaCl_2} + H_2O + CO_2.$$

The gas may be collected over water, or it may be led to the bottom of a gas jar and allowed to displace the air. (This method is possible because of the high density of carbon dioxide.)

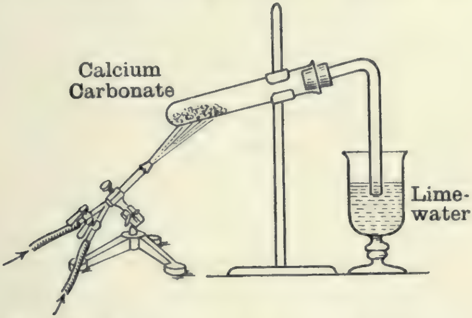


FIG. 77.—PREPARATION OF CARBON DIOXIDE.

2. The gas may also be obtained by strongly heating powdered limestone in a hard glass tube by means of a blowpipe (Fig. 77). If the gas given off be passed into lime water, the clear solution is turned "milky," showing it to be carbon dioxide:

$$CaCO_3 \underset{\text{strongly}}{\overset{\text{heated}}{=}} CaO + CO_2.$$

3. That the gas formed in the process of combustion is carbon dioxide can be shown by bubbling the products of combustion through lime water, when "milkiness" will be produced. A similar "milkiness" is obtained when expired air is bubbled through lime water, indicating that carbon dioxide is formed in the process of respiration.

Properties.—Carbon dioxide is a heavy, colourless, odourless gas, with a faintly acid taste. It neither burns nor supports combustion. The high density (heaviness) of the gas may be shown by pouring it into a balanced beaker (Fig. 78). The arm of the balance carrying the beaker is depressed, showing the gas to be heavier than the air originally in the beaker. At ordinary temperatures (60° F.) and pressures (30 inches barometer) water dissolves its own volume of the gas, yielding a faintly acid solution. The gas, being somewhat acidic in nature, is therefore absorbed readily by alkalies, such as caustic potash, caustic soda, lime, etc. (see pp. 132 and 134), in each case a carbonate being formed. When carbon dioxide is bubbled through lime water a precipitate of calcium carbonate is first obtained (which results in the lime water becoming "milky"), *calcium carbonate being insoluble.* If, however, carbon dioxide is bubbled through the lime water *for some time,* the "milkiness" gradually disappears and the solution becomes clear, as at the start. This is due to the conversion of the calcium carbonate into *calcium bicarbonate, which is soluble.*

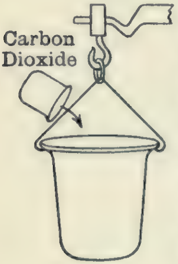


FIG. 78.

The precipitation of the calcium carbonate (the cause of the milkiness) is indicated in the equation—

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 = \underset{\substack{\text{Calcium carbonate}\\\text{(which is insoluble)}}}{CaCO_3} + H_2O.$$

The clearing or clarifying of the solution, by passing further carbon dioxide through the milky liquid, is indicated thus:

$$CaCO_3 + H_2O + CO_2 = \underset{\substack{\text{Calcium bicarbonate}\\\text{(which is soluble)}}}{Ca(HCO_3)_2}.$$

The above is sometimes expressed in another way, calcium carbonate being said to be soluble in water containing carbon dioxide. Now rain water always contains carbon dioxide, and it is continually falling upon large areas of soil underlain by chalk or by limestone, to which it finds its way. The calcium carbonate of such deposits is therefore being continually dissolved away as bicarbonate, sometimes to be deposited again as carbonate in the form of stalactites or stalagmites or simply as crystals of calcite, and sometimes to be retained in the water until it becomes mixed with the supplies used for domestic purposes or for steam-raising. Such water is "hard," and if used for steam-raising will yield much scale in the boiler and (see p. 214).

In the mine carbon dioxide, besides being formed by the breathing of men and animals and by the burning of lamps and candles, is given off in small quantities commonly with methane in firedamps from the coal and the associated strata either steadily or as blowers. In addition, the small coal in the waste is particularly subject to oxidation, the oxygen of the air being absorbed by the coal and converted either wholly or in part to carbon dioxide.* This gives rise to **blackdamp,** which consists of a mixture of carbon dioxide and nitrogen, the carbon dioxide being present as a rule to the extent of 5 to 20 per cent. (see p. 176). The nitrogen is merely the residual nitrogen of the air, the oxygen of which has been absorbed and converted, in part, at all events, into carbon dioxide.

The mine air, according to the C.M.A., must not contain more than $1\frac{1}{4}$ per cent. carbon dioxide. Carbon dioxide also occurs in the afterdamp of explosions (see p. 176).

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* In one instance the oxygen content of the intake air was reduced by 0·9 per cent. in 3,000 yards, due to oxidation of the small coal on the roadways.

CHAPTER XII

COMBUSTION, RESPIRATION, AND EXPLOSION.

Combustion.—It has been seen that when substances burn in air they combine with oxygen. The process is known as combustion. Combustion, however, covers a wider ground and comprises all chemical actions which take place with the evolution of light and heat. Thus various metals burn in chlorine gas to form chlorides, though the vast majority of cases of combustion involve combination with oxygen.

Flame is incandescent gas and is a visible indication of the area over which combustion is rapidly taking place.

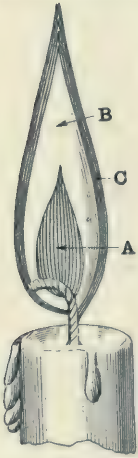

FIG. 79.—STRUCTURE OF CANDLE FLAME.

The structure of a **candle flame** is illustrated in Fig. 79. There are three zones —the inner non-luminous zone, *A*, the intermediate or luminous zone, *B*, and the third thin non-luminous zone, *C*, of complete combustion. In *A* no combustion takes place, and if one end of a piece of glass tubing be inserted into this zone the gases may be burnt at the other end of the tubing a short distance away from the candle. Paraffin wax consists essentially of a mixture of the higher members of the methane series (see p. 190) with a small amount of unsaturated bodies belonging to the olefine series, C_nH_{2n} (see p. 191). When these hydrocarbons are burnt, acetylene C_2H_2, is formed, together with some methane, CH_4, which gases are themselves combustible. When acetylene burns great heat is developed and the acetylene is split up into carbon and hydrogen. The luminosity of a flame is thought to be due, therefore, to incandescent solid carbon particles whose temperature is maintained (1) by the decomposition of the acetylene (which is an endothermic compound and therefore gives out heat on decomposition); (2) by the burning of the hydrogen liberated; (3) by the combustion of solid carbon particles. These particles " burn " in three ways:

1. $2C + O_2 = 2CO$.
2. $C + H_2O = CO + H_2$.
3. $C + CO_2 = 2CO$.

[The water vapour (H_2O) is derived from the combustion of the hydrogen.] There is therefore formed carbon monoxide and hydrogen, and these gases are burnt to carbon dioxide and water respectively in the outer non-luminous envelope, *C*. The flame of an oil lamp is similar to that of a candle. The temperature of a candle flame in the luminous zone is over 1,000° C.

Bunsen Burner.—The principle of the Bunsen burner is as follows: Air is drawn in with the gas to be burnt so that, due to the presence of oxygen in the gas flame, there is complete combustion and a non-luminous flame is produced. The construction of a Bunsen burner will be followed from Fig. 80. The gas enters via a jet at *A* and air is drawn in at *B*. The gas and air are mixed in the tube *C* and the flame obtained at the top of *C* is of the well-known non-luminous variety employed not only in the laboratory but in incandescent burners, and may be seen when the mantle is removed; also in gas-cooking stoves, etc. If the air inlet holes at *B* are closed a luminous flame is obtained. If pure oxygen be supplied in place of air at *B* an exceptionally hot flame is obtained which is luminous. The luminosity of such a flame is probably due to incandescent gas particles. The diluting action of the inert nitrogen of the air in the ordinary Bunsen burner

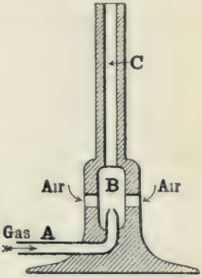

FIG. 80.—BUNSEN BURNER.

is therefore also responsible for the non-luminous nature of the Bunsen flame.

When incandescent gas mantles are employed the luminosity is due entirely to the incandescence of the mantle when raised to the requisite temperature. A gas mantle consists essentially of thorium oxide (99 per cent.) and cerium oxide (1 per cent.).

Combustion is merely relative. This may be shown in a variety of ways. A stream of air led into a jar of coal gas burns at a jet in the coal gas atmosphere exactly as does the coal gas in ordinary air. The experiment illustrated in Fig. 81 demonstrates this quite clearly. The gas is first turned on for half a minute in order to fill the lamp glass, and it is then lit at the hole in the asbestos sheet on the top. The flame is now extinguished by a duster which is pressed over the hole, and the gas passes out through tube *b*, where it burns on applying a light. The duster is then removed, and the flame travels back up tube *b* (a wide tube) and burns inside the glass, as shown. This flame is merely the air burning in an atmosphere of coal gas, the air being drawn in by the current of gas escaping at the top of the chimney, where it may be again lit. Thus, if the atmosphere we breathe had the composition of coal gas—or, rather, inflammable gas—we should keep oxygen in the gasometers and turn on the oxygen when we desired "to light the gas." (We assume that our constitutions could survive.) Moreover, we should say that oxygen was an inflammable gas, very explosive when mixed with certain quantities of other gases, and so forth. The terms "inflammable" and "supporter of combustion" therefore are purely relative, and used conventionally when

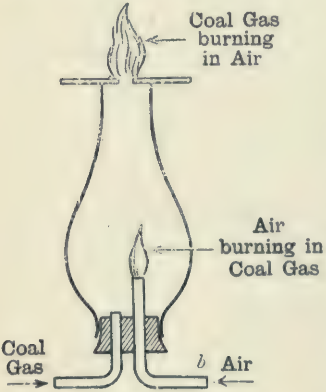

FIG. 81.

speaking of the behaviour of any gas or substance with regard to ordinary conditions.

The rate at which a substance combines with oxygen is very important. When a little iron burns in oxygen, the combustion or oxidation of the iron is complete in a few moments; but if the same amount of iron is allowed to rust in oxygen or air the complete oxidation or rusting may require several weeks. It is convenient here to state that the same amount of heat is evolved in either case, but in the rusting the heat is developed so slowly that it is carried away as it is produced, and therefore is not so apparent.

The rotting of timber also affords another example of slow oxidation, the carbon of the wood being gradually converted into carbon dioxide and the hydrogen of the wood to water (vapour). And again, as above, the same quantity of heat is evolved in the process of rotting as would be evolved by burning the timber. The complete combustion of carbon is represented by the equation—

$$C + O_2 = CO_2.$$

The complete combustion of hydrogen by the equation—

$$2H_2 + O_2 = 2H_2O.$$

The heat given out in these processes is utilised in the combustion of all commercial fuels, such as coal, coke, wood, gas, oils, peat, etc. (see p. 238).

Respiration.—When we breathe, air is taken into the lungs, and in the lung capillaries the oxygen of the inhaled air is absorbed by the "hæmoglobin" of the blood to form "oxyhæmoglobin." The hæmoglobin is the red colouring matter of the blood. Now blood charged with oxyhæmoglobin is circulated by the heart in the following manner: The heart is divided into four quarters, the two upper quarters being known as the right and left auricles, the two lower quarters being termed the right and left ventricles. From the left ventricle the blood (containing absorbed oxygen in the form of oxyhæmoglobin) is circulated into the principal artery,* thence into the minor arteries, and thence into the capillaries. From the capillaries the blood is returned to the veins, which lead it back to the right auricle of the heart. From the right auricle, the blood passes direct to the right ventricle, thence to the lung capillaries where it is "purified" (see later). It is finally returned to the left auricle of the heart and thence direct to the left ventricle, where the circulation is taken up and continued as before. The oxyhæmoglobin of the blood, on leaving the lungs, begins to part with its oxygen and continues to do so until it is exhausted. The oxidation of the tissues of the body is the result, and this is seen in the formation of carbon dioxide from the carbon of the body and of water from the hydrogen of the body. These are met with in the exhaled air, and the moisture also escapes by perspiration, etc. In order that the oxidation (combustion) of the body tissues may continue without detriment to the body, it is necessary to maintain a supply of further material (fuel) to replace the waste. This is done when food is taken.

Arterial blood, charged with oxyhæmoglobin, is bright red to scarlet; whereas venous blood, which contains much hæmoglobin *not* combined with oxygen, is dark red to purple. The processes which go on in the lungs are important. There is only a thin membrane partition between the air in the lungs and the lung capillaries, and through this partition gases can easily diffuse. The carbon dioxide brought to the lung capillaries by the venous blood diffuses through this membrane into the air of the lungs, and the air of the lungs diffuses in the opposite direction into the capillaries. The air in the lungs is only partially renewed at each breath, but enough of the carbon dioxide is expelled to enable the above process to continue without discomfort. Expired air from a deep breath contains by volume, neglecting moisture, about 79 per cent. nitrogen, 17 per cent. oxygen, and 4 per cent. carbon dioxide.

The whole process of respiration, therefore, is essentially

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* The arteries are the pipes or vessels which carry blood from the heart; the veins are the pipes which return the blood to the heart; the capillaries are a network of vessels connecting minor arteries and veins.

one of oxidation. It is this oxidation or slow combustion that maintains the heat of the body. Should this heat tend to increase, due to work, etc., perspiration follows, and the evaporation of this moisture from the skin has a beneficial effect in keeping down the temperature of the body.

Extinctive and Irrespirable Atmospheres.—A candle burning in a bell jar over water will be extinguished long before all—even before one-quarter—of the oxygen supply has been used up. When a candle burns, the carbon of the wax, etc., is converted to carbon dioxide, and the hydrogen to water, and these are the final chemical changes which occur. In the case of phosphorus burning in a limited supply of air, however, the whole of the oxygen is consumed. The difference in the behaviours of the phosphorus and the candle wax are due to the relative "affinities" or "likings" of phosphorus for oxygen on the one hand and of carbon and hydrogen for oxygen on the other. Now in breathing it is the carbon and hydrogen of the body which are combining with oxygen. Is it true, therefore, that atmospheres which extinguish a candle or oil flame are irrespirable ?

The following tables are compiled to show the effects of (1) *shortage of oxygen ;* (2) *presence of carbon dioxide ;* (3) *presence of carbon dioxide combined with a corresponding shortage of oxygen, which occurs in a limited atmosphere in which combustion or respiration has been taking place for some time.*

TABLE I.

% of O.	*% of N.*	*Effect on Man.*	*Effect on Flame.*
20·9	79·1	normal	normal
17·3	82·7	practically normal	burns with difficulty
15·0	85·0	,, ,,	flame extinguished
12·0	88·0	breathing deepens	
10·0	90·0	unusual shortness of breath: face flushed and darkened	
6·0	94·0	distinct panting, loss of consciousness, and finally death	
0·0	100	death with convulsions	

TABLE II.

% of CO_2.	% of Atmospheric Air.	*Effect on Man.*	*Effect on Flame.*
1·0	99·0	little or no effect	little or no effect
3·5	96·5	difficulty of breathing	small effect
6·0	94·0	marked panting and headache	flame somewhat dull
10·0	90·0	severe distress	flame duller
15·0	85·0	acts as a narcotic poison: partial loss of consciousness	flame extinguished
25·0	75·0	death in short time	

TABLE III.

% of CO_2.	% of O.	% of N.	*Effect on Man.*	*Effect on Flame.*
0·6	20·3	79·1	breathing deepens slightly	no effect
1·0	19·9	79·1	panting on exertion, and increase in frequency of pulse	burns somewhat dull
2·0	18·9	79·1	marked panting; face flushed; headache	dull, smoky flame
3.0	17·9	79·1	above symptoms more intense	flame extinguished
5·0	15·9	79·1	severe distress	
10·0	10·9	79·1	death in a few moments	

It is seen, therefore, that there is a very intimate connection between the burning of the oil in the lamp (or of hydrocarbons [see p. 189] in general) and the respiration of human beings and animals. Moreover, the combined effect of the shortage of oxygen and the presence of carbon dioxide, as seen in Table III., is much more intense than the effect of one or other of the above alone.

Explosions.—Coal gas, it is well known, may be lit at a jet and will burn quietly and regularly provided there is enough pressure behind it. (When this pressure is reduced sufficiently, the flame may " fire back " and a small explosion may ensue.) The quiet flame is only the visible indication of the *orderly* combustion of the gas—*i.e.*, of the combination of the gas with oxygen; and this combustion is maintained orderly by adjusting the *rate* at which it shall take place, by means of a tap, a jet, and a certain pressure. Hydrogen, we have seen, may be burnt at a jet in a similar fashion. If, however, a jar of hydrogen be mixed with a jar of oxygen (the gases will soon mix of their own accord, due to diffusion) and a source of heat—a lighted taper, say—be then introduced, an explosion ensues. The particles of each gas are in intimate contact, and the combustion, once started, is too rapid to permit of an orderly burning. This is the cause of all explosions; they are rapid, almost instantaneous, combustions. The necessary conditions are: (1) Combustible matter; (2) *ready* supply of oxygen; (3) shock or flame. The products of an explosion are gases at a high temperature, and therefore tending to occupy a large volume. If there is any opposition, huge pressures are developed. This is particularly true where solids or liquids explode to form gases, as the volume of such gases is, even if they were not heated to a high temperature, hundreds of times the volume of the original solid or liquid (see p. 219).

Coal Dust.—The explosion of methane in air is dealt with on p. 180. It has now long been recognised that *coal dust* of itself is highly explosive, and is particularly dangerous in its capacity for propagating an explosion, once started, throughout a mine, by continually supplying a cloud of such dust from the floor, roof, and sides of the roadways. Experiments have been carried out on a large scale at Altoft's and at Eskmeal's which prove beyond doubt the violent explosibility of coal dust, even where there is not a trace of inflammable gas (methane, etc.) in the air. The main conditions necessary for a coal-dust explosion are: (1) A cloud of the dust in a fine state of division; (2) a flame of sufficiently high temperature sent into the dust cloud; (3) the presence of air or of oxygen. The commonest causes of coal-dust explosions in mines are the vibrations and flames produced by " blown-out shots " and by local explosions of firedamp. Herein lies the principal danger of firedamp in that its local explosion may start an explosion of—or, in other words, may *detonate*—the coal dust in the mine; and herein also lies the danger of blasting in coal mines unless every precaution is taken in the location of the shot-holes, in the stemming or tamping, in testing for inflammable gas before firing, and finally in rendering the dust in the vicinity inexplosive by admixture with inert dust. To render coal dust inexplosive several suggestions have been made and experimented upon. Watering is not so satisfactory as might be thought, due to the difficulty of completely wetting the dust and also because of the continual evaporation of water; and in addition, the watering of the floor and sides of a dry mine often causes serious trouble with the strata, and the support of the roof and sides of the roadways becomes a matter of considerable difficulty and great expense. Moreover, the atmosphere of the mine becomes saturated with water vapour which, as has been seen, is harmful to the men at the high temperatures which sometimes prevail in mines. The most satisfactory method, so far, of rendering coal dust inexplosive is to mix with it sufficient finely-ground incombustible dust. Many of the shales met with in coal-measure strata yield suitable incombustible dusts when ground. In further experiments carried out at Altoft's and Eskmeal's on a large scale it was found that in the vast majority of cases, if the combustible matter in the mixed dusts was less than 50 per cent., the mixed dusts were inexplosive. The Regulations (dated July 30, 1920) of the Coal Mines Act, 1911, regarding coal dust state that in all coal mines, except anthracite mines, the floor, roof, and sides of every road shall, unless the natural conditions are such as to comply with the requirements, be treated in one or other of the following ways, either:

(*a*) With incombustible dust, so that the mixed dusts shall contain not more than 50 per cent. combustible matter.

(*b*) With water, so that the dust throughout is always mixed intimately with 30 per cent. by weight of water.

(*c*) In some other manner approved by the Secretary of State.

These Regulations relate to all roads except the area within 10 yards of the coal face, but do not apply to chutes from the coal face down which the coal is thrown, offices, stables, engine houses, motor switch, and transformer rooms and pump rooms. It is further laid down in the same Regulations that the incombustible dust used shall contain not less than 50 per cent. by weight of fine material capable when dry of passing a sieve of 200 meshes to the lineal inch (40,000 to the square inch). The incombustible dust must be at least of this degree of fineness if the sample of the treated mine dust contains 50 per cent. of combustible matter. A concession, however, is made; if there is less than 50 per cent. combustible matter, an incombustible dust may be used in which 50 per cent. will *not* pass through the 200-mesh sieve provided that the amount that *will* pass through is not less than the amount of combustible matter in the treated mine dust, and is in no case less than 25 per cent. [the dust sample is to be taken over a length of roadway of not less than 50 yards], and that part of the material which passes through a gauze of 28 meshes to the lineal inch (ordinary lamp gauze) is to be regarded as mine dust. The moisture in the dust is to be estimated by drying a weighed quantity at 212° F. and finding the loss in weight. The combustible matter is to be obtained by bringing the dried dust to a red heat in an open vessel and heating until there is no further loss in weight. The weight so lost by incineration is to be reckoned as the combustible matter. (For full details of the sampling, testing, and treatment of mine dusts, see *Coal Mine Dust*, by McMillan and Whitaker, published by T. Wall and Sons, Wigan.)

The testing of the dust is a comparatively simple matter, but it requires care, not only in the laboratory but in the sampling in the mine. It is all-important to have a representative sample, and this can be obtained in the mine only by exercising considerable discretion. The moisture is most conveniently estimated by weighing about 2 grams of dust in a weighed porcelain dish, and placing in a water-jacketed copper oven, the water being maintained boiling by a burner underneath (Fig. 82). The material should be removed from the oven after one hour, allowed to cool in a desiccator (see p. 244), and weighed when cold. It should then be replaced in the oven, and removed at half-hour intervals and allowed to cool, as above, the heating being continued until the material begins to gain in weight, due to oxidation. The lowest weight obtained is regarded as the weight of the dust when dry plus, of course, the weight of the porcelain dish. The percentage of moisture is thus easily calculated. The dish and contents are now heated strongly by one or two Bunsen burners or, preferably, in a muffle furnace with the front open. An occasional stirring assists the combustion of the organic portion, though care must be taken not to remove any material in the process. When all the carbonaceous matter has burnt off —which may take an hour or more—the dish and contents are allowed to cool in the desiccator and finally weighed. The loss in weight of the dish and dry dust is the weight of the combustible matter, and may easily be calculated as a percentage on the weight of the original (moist) mine dust.

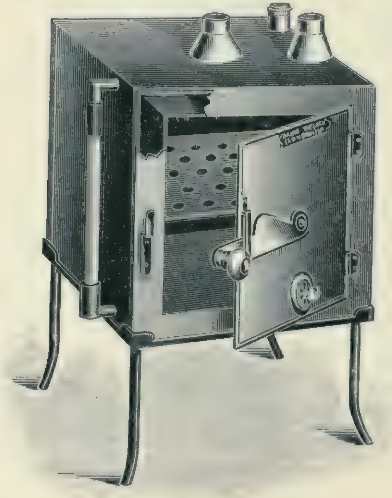


Fig. 82.—Water Oven.

The inert or incombustible dust used should not contain free silica particles owing to the action of such dusts on the lungs, causing fibrosis. Small angular particles of quartz silica are very irritating to the lung tissues, and the lungs soon tend to lose their aerating capacity due to the formation of dense nodules of fibrous growth. The individual is thus rendered easily susceptible to tubercular infection, so that tuberculosis frequently follows fibrosis.

Note.—1. Special Regulations deal with the testing of mine dusts which have been treated with a stone dust containing carbonates—such as limestone—since, on ignition, carbonates are decomposed, carbon dioxide being given off (see p. 159).

Note.—2. Anthracite dust is not explosive. In general, though there are exceptions, a coal dust is more liable to explosion according as it contains more volatile matter. " Volatile matter " is a somewhat loose phrase, but refers to the approximate amount of volatile vapours expelled when a coal or coal dust or the like is coked or roasted at a red-hot temperature without allowing any access of air. The pressure is supposed to be normal. Exactly why one coal dust is more explosive than another is not known. No doubt it is governed by the size of the dust, the fineness, the specific gravity, the ash content, and so forth; but it is also dependent upon the constitution of the substances composing the coal, about which little definite is known.

Spontaneous Combustion.—The rate of oxidation of combustible bodies, even when they are not burning, is increased by rise in temperature. That temperature at which a body begins to burn is called its " ignition-point." If a substance, on beginning to burn, gives out sufficient heat to maintain the temperature above the ignition-point, combustion will proceed until all the substance has been burned, even though the original source of heat be removed. On the other hand, if the heat developed in the burning is insufficient to maintain the temperature above the ignition-point, the process will cease when the source of heat is removed. It is clear that only substances of the former class—*i.e.*, substances which *do* emit sufficient heat—can be used as fuels.

Now, in the slow oxidation which proceeds when certain substances are left in air (such as the " rotting " of timber, the " weathering " of coal, the absorption of oxygen by phosphorus, the rusting of iron, and so forth), a certain amount of heat is always developed; and, unless this heat is carried away, the temperature rises. With rise in temperature the rate of oxidation increases, which causes further rise in temperature, and consequently further oxidation, until finally the ignition-point is reached and the substance takes fire of its own accord. This is known as "spontaneous combustion." Spontaneous combustion is therefore encouraged if—

1. The substance has a great affinity for oxygen.
2. There is a fairly good supply of air, but not so much as to carry away the bulk of the heat developed.
3. If there is a large surface of the substance exposed to the air, which is true when the substance is in a small form, almost powdery.
4. If the ignition-point of the substance is low.
5. If the substance is surrounded by material which is not a good conductor of heat.

Spontaneous Combustion of Coal.—Freshly exposed coal absorbs oxygen from the air. Certain coals absorb more oxygen than do others, some absorbing more than three times their own volume, the gas being measured at ordinary temperatures and pressures. At the same time there is no corresponding amount of carbon dioxide or of water formed, so that the action is thought to be one of "occlusion" in the first instance, at any rate. This occlusion or absorption of oxygen results in the compression of the gas, and when a gas is compressed the temperature tends to rise. Moreover, the gas so absorbed is in a more chemically active form than the free gas. It is not surprising, therefore, that oxidation begins to take place often very rapidly, the temperature rises, further oxidation ensues with further rise in temperature, until the ignition-point (400° C. approx.) of the coal is reached and the material takes fire. This is particularly common where the nature of the coal and the other four conditions mentioned above are favourable. The influence of pyrites in causing spontaneous combustion of the coal in which the pyrites occurs is discussed on p. 143. Coal itself is a bad conductor of heat, which further assists its spontaneous combustion in large heaps.

The presence of moisture in small amount appears to assist in the heating.

In order to prevent spontaneous combustion in coal mines there should be as little coal left in waste or gob as possible; the waste should be well "packed" or "stowed" to prevent the circulation of air therein, and any seams within a few feet of the seam being worked should, if possible, be worked at the same time. Hydraulic stowing of the waste is a sure remedy, but this method of stowing has not found much favour in Britain, due largely to the expense. Should a gob fire break out, the manner of treatment depends upon the size of the fire and the conditions generally. If it is only local heating, it may be dug out, quenched, and sent out of the mine. If it is a large outbreak and the conditions permit of the flooding of the district with water without undue losses, such a course may be best. In other cases it may be advisable to build off the fire with brick stoppings well packed with sand, etc., and so extinguish the fire by cutting off the air supply. Periodical analyses of the atmosphere on the other side of the stoppings should be made in order to follow the course of the combustion, and so that samples of such atmosphere may be taken, iron pipes with valves should be built in at the time the stoppings are being erected. Flooding the affected area with carbon dioxide gas has also proved effective in some instances. Carbon dioxide is easily obtained under pressure—in the liquid form if desired—and, being a heavy gas, does not readily diffuse from the neighbourhood in which it is liberated. It has an advantage over water flooding as the latter frequently causes trouble with the roadways, roof, etc., sometimes necessitating entirely fresh roads.

The air in the neighbourhood of a gob fire may be expected to contain a fair amount of CO_2 (say 4 per cent.), a dangerous quantity of CO (say 1 per cent.), a little CH_4 (say 0·5 per cent.), and a much reduced oxygen content (say 15 per cent.). A trace of hydrogen may also be present. The above figures are by no means constant, nor may they even be taken as general averages. They are given merely as sample figures obtained in a few analyses from different places.

CHAPTER XIII

MINE GASES.

THESE comprise nitrogen, oxygen, carbon dioxide, carbon monoxide, methane, and sulphuretted hydrogen. Traces are also found of ethane and propane, ethylene, acetylene, and sulphur dioxide.

In mining language the various gases, either as mixtures or individually, are called " damps."

" Firedamp " is a mixture of gases containing from 60 to 100 per cent. methane, with varying amounts of carbon dioxide and other gases.

" Blackdamp " or " chokedamp " is usually a mixture of nitrogen and carbon dioxide containing up to 20 per cent. of carbon dioxide: an average composition is about 90 per cent. nitrogen with 10 per cent. carbon dioxide (see p. 161). The term " blackdamp " is also applied to any mixture of gases which will extinguish a lamp and is not explosive and, when diluted with sufficient air to allow the lamp to burn, is not poisonous. " Afterdamp " is the mixture of gases left after an underground explosion, and has a somewhat similar composition to that of blackdamp. If, however, coal dust has taken part in the explosion—and in all large mine explosions coal dust does take part—a certain amount of carbon monoxide (averaging about 3 per cent.) will be found in the afterdamp.

" Whitedamp " is the mining term for carbon monoxide.

" Stinkdamp " is the mining term for sulphuretted hydrogen.

Oxygen, nitrogen, and carbon dioxide have already been discussed.

Methane, CH_4.

Molecular weight $= 16$; density $= 8$; specific gravity $= 0{\cdot}56$.

Methane is also known as Marsh Gas and as Light Carburetted Hydrogen. It is the chief constituent of firedamp, present as a rule to the extent of 60 to 100 per cent.

Occurrence and Formation.—1. Methane is formed when vegetable matter decays and decomposes under water. Cellulose is the principal constituent of wood fibre and of vegetable matter in general, and under the influence of certain bacteria the cellulose of the decaying matter "ferments," gases, chiefly methane and carbon dioxide, being liberated. Cellulose is an organic substance of complex constitution; its chemical molecular formula is indicated by $(C_6H_{10}O_5)_n$, where n is as yet an unknown number. The chemical changes produced by the bacterial fermentation of cellulose may be represented by the equation—

$$2C_6H_{10}O_5 = 5CO_2 + 5CH_4 + 2C.$$

The origin of the methane found in the firedamp of coal mines is clearly suggested. The early vegetation, from which the coal has been formed, "decayed" in swampy ground, methane being set free. The greater part probably escaped, but on the submergence of the decaying vegetable matter the bacterial processes would not be arrested immediately, and the gases would accumulate unless the overlying sediments were sufficiently porous. In the course of ages, the weight of the overlying strata increasing, and the earth's crust continually contracting (due to cooling), the pressures under which these gases were held or pent up increased, sometimes to an enormous extent, and the blowers of firedamp now met with in the underground workings are merely the outcome of the whole process. Methane is often given off from the coal at the face due to the fact that coal under pressure absorbs or, rather, occludes methane. On reduction of the pressure—which occurs when a new face is exposed, the original high pressure being reduced to atmospheric—the occluded gas is evolved.

2. Methane is also formed by the distillation of coal, as in coke-oven plant and gas retorts. It forms about 33 per cent. of ordinary coal gas, the rest being mainly hydrogen with small quantities of carbon monoxide, carbon dioxide, etc. It is possible, therefore, that some of the firedamp found in mines may have been derived from the natural distillation of the coal in the earth's crust, particularly in much-faulted ground where the heat developed by dislocations of the strata is additional to the heat from the earth's interior. It is interesting in this respect to note that on gently distilling coal the methane and oxides of carbon are given off more readily than the hydrogen at low temperatures, the hydrogen coming off principally at high temperatures. This, and the lightness and rapid diffusion of hydrogen, may account for the absence of hydrogen in firedamps formed in the above manner; but it should be borne in mind in explaining the frequent association of firedamp with faults that the latter are often of a close, glassy, impervious texture, and consequently form a barrier through which the gases formed—either by the fermentation process or by distillation—cannot diffuse. It is therefore to be expected that in such places there will be a concentration of the gases, whether there has been any appreciable heating or not.

It will be noticed in the analyses of firedamps given on p. 183 that there is often some CO_2 present, which is in agreement with both of the above theories of origin.

Preparation of Methane.—1. Heat a mixture of sodium acetate ($CH_3.COONa$) and caustic soda. Quicklime, in addition, is often used to assist the operation. The experiment is best carried out in a metal flask, as a rather high temperature is necessary:

$$CH_3.COONa + NaOH = Na_2CO_3 + CH_4.$$

The apparatus is shown in Fig. 83, the gas being collected over water.

2. A more convenient method of preparation is to collect

the gas given off by the action of water on aluminium carbide, Al_4C_3. This gas is fairly pure methane:

$$Al_4C_3 + 12H_2O = 3CH_4 + \underset{\text{Aluminium hydroxide}}{4Al(OH)_3}.$$

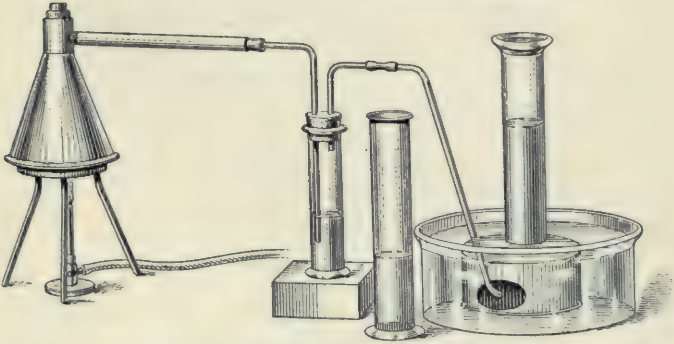


FIG. 83.—PREPARATION OF METHANE.

The apparatus required is indicated in Fig. 84. It is usually necessary to warm the water, but any heating should be done very cautiously, as large volumes of the gas tend to be liberated suddenly.

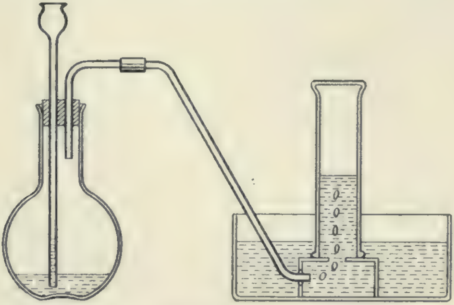


FIG. 84.—PREPARATION OF METHANE.

Note.—This method is similar to the method commonly employed for the preparation of acetylene—as in the acetylene lamp—water being allowed to act on calcium carbide:

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Acetylene}}{C_2H_2} + \underset{\text{Slaked lime or calcium hydroxide}}{Ca(OH)_2}.$$

Properties.—Methane is a colourless, odourless, tasteless gas. It is not poisonous. It is very slightly soluble in water. Methane does not support combustion, but is itself highly inflammable in air, and when mixed with suitable proportions of air or of oxygen it is violently explosive. The maximum rate of explosion is obtained when 1 volume of methane mixed with 2 volumes of oxygen (or 9·4 volumes of air) is ignited. The explosion in oxygen is indicated by the equation—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The explosion in air may be *roughly* denoted thus:

$$CH_4 + 2O_2[+8N_2] = CO_2 + 2H_2O[+8N_2].$$

It is not correct to write the amount of nitrogen as $8N_2$. It is more nearly $(2 \times \frac{79}{21})N_2$—and this neglects argon, etc. The above equation, however, is approximate, and indicates that the afterdamp from a pure methane explosion in air consists of nitrogen, carbon dioxide, and moisture—plus, of course, any excess of oxygen present. If there were a shortage of oxygen, carbon monoxide would be formed. Most afterdamps contain carbon monoxide, but this is due to the insufficient oxygen for a "complete" coal-dust explosion:

$$\begin{aligned} 2C + O_2 &= 2CO \text{ (incomplete)} \\ 2C + 2O_2 &= 2CO_2 \text{ (complete).} \end{aligned}$$

In a methane explosion the water formed is at first for an instant present as steam, but the steam rapidly condenses and the temperature of the gases rapidly falls. There is, therefore, in an explosion first an outrush of gases from the source of the explosion followed by an inrush, or "after-blast," caused by the fall in temperature and the condensation of the steam, which produce a "partial vacuum."

The behaviour of mixtures of methane and air on introducing a light or source of heat may be seen from the following. For convenience an electric arc may be sent from one pole to another in the mixture in question, but the behaviour is identical with an ordinary flame.

Per Cent. Methane.	*Effect.*
2·0	The gas burns around (on top of) the source of heat only so long as the source of heat is in the mixture.
3·0	Behaviour as above, but the gas burns over a slightly greater area round the source of heat.
4·0	Behaviour as with 3·0 per cent. CH_4, but gas burns over a still greater area round the source of heat.
5·0	Behaviour as with 4·0 per cent. CH_4, only still more marked burning of the gas.
5·6	The flame passes throughout the mixture even though the source of heat be removed immediately after ignition.
7·0	A weak explosion occurs, which is more violent with increasing amounts of CH_4 till there is 9·4 per cent. CH_4 present.
9·4	A violent explosion occurs; this yields the maximum rate of explosion. It is the most violently explosive mixture attainable with methane and air. With increasing amounts of methane the rate of explosion and the explosive violence are reduced.
15·0	The flame ceases to pass of its own accord throughout the mixture, as in the cases where the methane is less than 5·6 per cent.
20·0	The gas burns around the source of heat only so long as the latter is in the mixture.
25·0	The flame is extinguished.

The "**explosive range**" is seen to lie in mixtures of air and methane containing between 5·6 and 15 per cent. methane, and any such mixtures are known as "**inflammable mixtures.**" An inflammable mixture is a mixture of gases throughout which a flame will travel away from and independently of the source of ignition; 5·6 per cent. of methane in air is known as the **Lower Limit of Inflammation,** and 15·0 per cent. of methane in air is known as the **Upper Limit of Inflammation.**

"**Caps.**"—When a flame is introduced into a mixture of methane and air containing less than 5·6 per cent. methane, a pale blue " cap " or " halo " is formed on top of the flame. It appears as a separate division of the same flame if the (original) flame be lowered enough to remove *almost* all luminosity. This cap is caused by the burning of the methane immediately near the source of heat, for here the temperature is high enough to ignite the CH_4 particles. (The ignition-point of methane in air is about 700° C.) The CH_4 particles themselves in burning generate a certain amount of heat, which they pass on by convection currents to the CH_4 particles above; but the heat generated is only sufficient to extend over a *small* volume at a high temperature and the size of the cap is therefore limited. If, however, the methane particles are closer together—which they are as the percentage of methane in the mixture increases—more of the heat is available for causing them to ignite, as there are fewer associated particles of inert gas to be heated at the same time. Moreover, still further heat is generated because of the combustion of more methane particles. In consequence, the size of the cap rapidly increases (see p. 186) with small increases in the percentage of methane, until a point is reached when the heat produced by the combustion of the methane near the flame is sufficient to raise the surrounding methane to its ignition-point (700° C.), and the flame is propagated throughout the mixture without any necessity for the continued presence of the initial source of heat. This occurs when 5·6 per cent. methane is present, and this, as has been said, is known as the **Lower Limit of Inflammation** of methane in air.

Ethane and **Propane,** sometimes found in small amounts in firedamp, have the Lower Limits of Inflammation and **Ignition Temperatures** indicated below:

Gas.	*Lower Limit of Inflammation in Air.*	*Approximate Ignition-Point in ° C.*	
		In Oxygen.	*In Air.*
Methane (CH_4) ..	5·60	556–700	650–750
Ethane (C_2H_6) ..	3·15	520–630	
Propane (C_3H_8) ..	2·18	490–570	

It is clear that if a firedamp contains any ethane or propane the Lower Limit of Inflammation of the firedamp will be lower than that of pure methane; but as ethane, propane, etc., occur only in very small amounts the difference is not likely to be appreciable.

OCCURRENCE OF METHANE IN THE FIREDAMPS OF COAL MINES.

Analyses of some typical firedamps are given below:

	I	II	III	IV	V	VI	VII
Methane (CH_4) ..	77·5	95·0	86·5	97·3	83·1	95·4	79·84
Nitrogen (N)	21·2	0·7	11·9	2·3	14·4	4·0	14·36
Oxygen (O)	—	—	—	—	0·4	—	—
Carbon dioxide (CO_2)	1·3	4·3	1·6	0·4	2·1	0·6	3·90
Ethane (C_2H_6) ..	—	—	—	—	—	—	1·90

Methane, being a light gas, tends to accumulate near the roof and in the rise workings of the mine. It is often found at the face of the "ripping" or "brushing," and in cavities or fissures in the roof. It continually diffuses into the air below, but sometimes the rate of diffusion is too slow, and the air current has to be directed in among the gas accumulation. This is done by arranging canvas or brattice cloths to check the flow of air along the lower half of the roadway and so concentrate the air current near the roof.

According to the C.M.A., 1911, the men must be withdrawn from any place in which the percentage of inflammable gas in the main body of the air exceeds 2·5, and the place must be fenced off in all means of ingress. If there is more than 1¼ per cent. of inflammable gas in the air current, all electric machinery must be stopped.

Only locked safety lamps may be used in any seam if the air in the return airway from any ventilating district contains normally more than 0·5 per cent. of inflammable gas. Where naked lights are commonly used, safety lamps must be substituted if the percentage of inflammable gas in any place rises to 1·25, or the men must be temporarily withdrawn.

Gas Caps and Testing for Inflammable Gas.—The inflammable portion of firedamp is, as has been seen, practically all methane. The following results, therefore, based on mixtures of methane and air, are a reliable guide. When a flame is introduced into such a mixture (containing less than 5·6 per cent. methane) a cap or halo is produced, and the *size* of this cap or halo is, if the flame itself is of a standard size and heating value, a fairly accurate measure of the amount of methane present. Lest the amount of methane should exceed 5·6 per cent. the flame is surrounded by one or more wire gauzes, in order that if any ignition of gas takes place, the ignition may be confined to the lamp. As was seen on p. 68, the flame when such ignition takes place does not pass through the gauze, due to the fact that the heat is conducted away so rapidly by the metal of the gauze; and as a general rule the light is extinguished, due to the interference with the air currents (convection) in the lamp. There are many types of miners' safety lamps, but the commonest are adaptations of the Marsaut, the Meuseler, and so forth, each type having slight modifications of the above principle. In each lamp there is an arrangement for raising or lowering the flame.

In the mine, when testing for firedamp, first *gradually* introduce the lamp into the suspected atmosphere with the flame burning about half the ordinary size. If there is above 3 per cent. inflammable gas present, the flame will tend to grow taller and taller. If this is observed, the lamp should be cautiously removed from the dangerous zone else the gas may "fire" in the lamp, and, if the gauze is in any way defective, a serious mine explosion may result. There is no greater foolishness than to encourage "gas" to fire in the lamp; it is equal to striking a match in an explosive magazine, and relying on no accident occurring.

If no such elongation of the flame is observed, the flame is lowered to a "testing flame." This is usually obtained when the flame can be lowered no further without being extinguished. It should be about $\frac{1}{10}$ of an inch high and $\frac{3}{8}$ of an inch broad and should be nearly non-luminous. If this flame be now examined in ordinary air a very small and indistinct cap may be seen along the upper edges of the flame. This is known as the "fuel cap," and must not be confused with the gas caps described below. The gas caps are quite distinct to any observer with normal eyesight who examines the cap carefully. The lamp is now introduced into the suspected atmosphere, and after about half a minute the flame is observed carefully. If there is no more than the original fuel cap visible, the atmosphere contains much less than 2 per cent. of inflammable gas. If, however, a larger cap is visible the amount of inflammable gas present may be estimated fairly accurately from the size of the cap. The size of the cap is but little affected by the quality of the ordinary lamp oils, provided that the breadths and heights of the testing flames are approximately true—$\frac{3}{8}$ inch broad and $\frac{1}{10}$ inch high.

LABORATORY AND MINE TESTS WITH STANDARD TESTING FLAME.

Sir John Cadman's Results in Laboratory.		**Dr. Gray's Results from Samples taken in the Mine.**	
Per Cent. CH_4.	*Height of Cap in Inches.*	*Per Cent. CH_4 on Analysis.*	*Height of Cap in Inches.*
2·0	0·25	2·01	$\frac{1}{4}=0·25$
2·5	0·35	3·28	$\frac{3}{8}=0·375$
3·0	0·50	3·44	$\frac{1}{2}=0·50$
3·5	0·75	3·64	$\frac{3}{4}=0·75$
4·0	1·25	4·13	$1\frac{1}{4}=1·25$
4·5	Top of glass	—	—
5·0	Gas caps cease	—	—

In Fig. 85 is given a graph showing the height of the cap on a standard flame with varying percentages of methane in air.

The size of the testing flame is important. If it is increased, the heights of the caps are increased (due to the additional heat), but when it becomes too luminous the caps are not easily seen. On the standard testing flame when less than 2 per cent. CH_4 is present, the cap is not fully formed and has no visible apex. High temperatures in the mine have a slight effect on the size of the caps, especially if a light mineral oil (such as "colzaline," which is practically "benzine") is being used in the lamp. In such cases the caps in a hot atmosphere tend to be somewhat larger than those indicated for the same percentages of CH_4 in the cold, so that an atmosphere might be thought to have a 2·5 per cent. CH_4 content from the cap test, whereas rather less than 2 per cent. CH_4 might be found on analysis. However, this is an error on the right side. It has been suggested that changes in the barometric pressure may appreciably influence the height of the cap obtainable with a certain percentage of CH_4, but there is no justification for the suggestion, the influence of the barometric pressure changes on the caps being negligibly small.

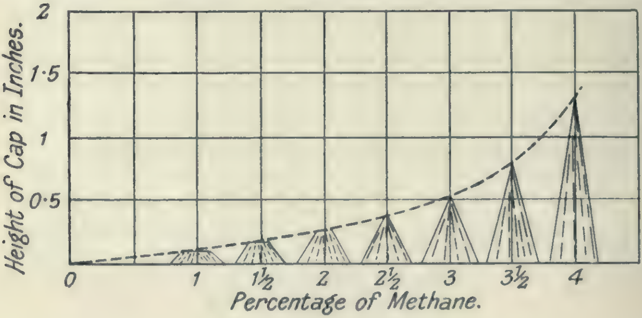


FIG. 85.—GAS CAPS.

Special Gas-Testing Lamps and Devices.

Several devices have been brought forward to enable small quantities of methane or inflammable gas in air to be accurately estimated, but all without exception have serious disadvantages. Indeed, it is to be doubted whether more reliable results cannot be obtained with the ordinary miner's safety lamp provided that the flame is capable of being lowered to the requisite degree. In the hands of an experienced person it is possible, with the ordinary safety lamp, to detect—and estimate fairly accurately—amounts of CH_4 as small as 1 per cent., but care and experience and good eyesight are necessary.

The following are some of the commoner special gas-testing devices: Clowes' Hydrogen Lamp; Stokes' Alcohol Lamp; Beard-Mackie Indicator; Brigg's Loop.

Clowes' Hydrogen Lamp is an ordinary Heppelwhite-Gray lamp with a long glass—in order that the long caps obtained may be seen—and with a cylinder of compressed hydrogen capable of being fitted alongside the lamp. Ordinarily the lamp burns oil, but when it is desired to test for " gas " the hydrogen cylinder is connected up, the hydrogen turned on, and lit at a jet in the lamp from the oil flame. The oil flame is then extinguished by drawing down the wick, and the hydrogen flame adjusted to a certain standard height marked on a scale inside the lamp. Hydrogen burns with a blue intensely hot flame to form (steam) water. It is on account of the heat developed that the caps formed—when any methane is present—on the hydrogen flame are much larger than those formed on an ordinary oil flame. The amount of "gas" present is indicated by the height of the cap, and this is read off on the scale already mentioned, which may be graduated to read directly the percentages of inflammable gas. The disadvantages of the apparatus are: (1) The steam formed by the burning of the hydrogen condenses to water on the lamp glass, causing the latter to become "misty." It is difficult under such conditions to estimate the true height of the cap. (2) A slight variation in the quality of the hydrogen makes a considerable difference to the size of the cap obtained. (3) Due to the danger of having a hydrogen explosion in the lamp, the lamp is not permitted in " safety-lamp " mines.

Stokes' Alcohol Lamp.—In this lamp use is made of the fact that alcohol burns with a blue non-luminous flame, and if used in place of ordinary lamp oil will yield visible (and larger) caps without the necessity of lowering the flame to the same degree. The alcohol, however, must be perfectly pure, otherwise the percentages of methane as indicated by the caps are unreliable.

Beard-Mackie Indicator.—This consists of a small ladder with platinum-wire rungs supported vertically above the flame so that only the lowest rung of wire is red hot when the flame is at its ordinary height. If there be any small amount of methane present, the cap formed, but not visible, due to the luminosity of the lamp flame, causes one or more of the lower rungs of platinum wire to become hot and to glow. This is due to the heat developed by the combustion of the methane, which combustion tends to be concentrated on the surface of the platinum wire. The greater the number of bright red-hot rungs, the greater the percentage of methane. It is a simple matter to graduate the apparatus in air and methane mixtures of known CH_4 content, and so make the indicator direct reading. The Beard-Mackie Indicator is one of the most satisfactory of the devices mentioned, but it has the disadvantage that the carbon from the flame soon blackens the platinum wire which, in consequence, does not brighten with heat as it normally does.

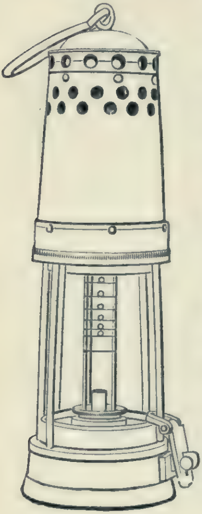


Fig. 86.—Miner's Lamp with Beard-Mackie Indicator.

Brigg's Loop.—This is a simple contrivance. It consists of a simple copper-wire loop which passes through to the lamp bottom in much the same way as does an ordinary wick-adjuster or pricker. The loop, however, is capable of being placed over and round the flame, thereby lowering the temperature below incandescence and causing the gas cap to show up more distinctly even with very small amounts. Great skill and experience are necessary, as the ordinary fuel cap is increased by the copper loop, and an *apparent* gas cap is seen when no inflammable gas is present.

The other devices for detecting methane in small amounts, such as the Liveing Indicator, the Cunnynghame-Cadman Device, and the Ansell's Diffusion Indicator, are of little practical importance, and the reader is referred to *Detection of*

Inflammable Vapour, by Clowes and Redwood, for their description.

Analysis of Gases for CH_4 (see p. 153).—In the laboratory methane is estimated by burning a known volume of the gaseous mixture and first measuring the contraction, X, due to the formation of water, and secondly finding the amount, Y, of CO_2 formed in the above burning by absorbing the CO_2 in caustic potash solution and measuring the volume of the unabsorbed gases. It is, of course, necessary to have sufficient oxygen present in the gaseous mixture to permit of the complete burning of the CH_4 in accordance with the equation—

$$\underset{\text{1 volume}}{CH_4} + \underset{\text{2 volumes}}{2O_2} = \underset{\text{1 volume}}{CO_2} + \underset{\substack{\text{2 volumes} \\ \text{(as vapour)}}}{2H_2O}.$$

The 2 volumes of H_2O, however, condense immediately to liquid water and the volume of the water thus obtained is negligible. There is therefore a contraction equal to twice the volume of the methane. Moreover, the CO_2 formed is equal in volume to the methane. This provides a check on the figure as obtained from the contraction. In the above symbols the volume of $CH_4 = \frac{X}{2} = Y$.

If other combustible gases are present the calculation is more complicated; such other gases are best removed before the methane is burned.

Methane and Its Relation to Petroleum.—Methane is the simplest member or " prototype " of a large number of hydrocarbons similar to it in many ways, particularly in their chemical stability. On account of this unreadiness to react with most ordinary chemical substances they are called the **paraffin family.** (*Par* = little; *affinis* = affinity.) Most of these hydrocarbons are found in crude **American petroleum.** They are thought to be the result of the decomposition of cellulose under somewhat different conditions from those which gave rise to coal and firedamp. Natural gas (mainly methane) is often tapped at the same time as petroleum. The hydrocarbons of the paraffin series from methane downwards have the general formula, C_nH_{2n+2}.

TABLE OF THE PARAFFINS

Formula.	*Name.*	*Melting-Point in ° C.*	*Boiling-Point in ° C.*	*Specific Gravity.*
CH_4	Methane	–186	–164	0·415 at b.-pt.
C_2H_6	Ethane	–172	– 90	0·446 at 0° C.
C_3H_8	Propane	—	– 38	0·536 ,, ,,
C_4H_{10}	Normal Butane	—	+ 1	0·600 ,, ,,
C_5H_{12}	,, Pentane	—	+ 36	0·633 at 15° C.
C_6H_{14}	,, Hexane	—	69	0·677 at 0° C.
C_7H_{16}	,, Heptane	—	98	0·700 at 0° C.
C_8H_{18}	Octane	—	125	0·718 ,, ,,
C_9H_{20}	Nonane	—	150	0·733 ,, ,,
$C_{10}H_{22}$	Decane	—	173	0·745 ,, ,,
$C_{11}H_{24}$	Undecane	—	195	about 0·75 to 0·78.
$C_{12}H_{26}$	Duodecane	—	214	
$C_{13}H_{28}$	Tridecane	—	234	
$C_{14}H_{30}$	Tetradecane	—	252	
$C_{15}H_{32}$	Pentadecane	—	270	
$C_{16}H_{34}$	Hexadecane	18	287	All about 0·78 at their melting-points.
$C_{17}H_{36}$	Heptadecane	22	303	
$C_{18}H_{38}$	Octadecane	28	317	
$C_{19}H_{40}$	Nonadecane	32	330	
$C_{20}H_{42}$	Eicosane	37	205 Boiling under pressure reduced to 15 mm.	
$C_{21}H_{44}$	Heneicosane	40	215	
$C_{22}H_{46}$	Docosane	44	224	
$C_{23}H_{48}$	Tricosane	48	234	
$C_{24}H_{50}$	Tetracosane	51	243	
$C_{27}H_{56}$	Heptacosane	60	270	
$C_{31}H_{64}$	Hentriacontane	68	302	
$C_{32}H_{66}$	Dotriacontane	70	310	
$C_{35}H_{72}$	Pentatriacontane	75	331	

The first four of the above series are gases at ordinary temperatures and pressures. Pentane and hexane are light volatile liquids, and the succeeding members are first similar volatile liquids, but they rapidly become less volatile, more viscous, and more dense (heavier bulk for bulk). They are obtained as mixtures from petroleum by fractional distillation —*i.e.*, by distilling carefully and condensing the vapours that are given off at the various temperatures. It is necessary to redistil the "fractions" obtained from a first distillation in order to obtain the commercial products.

Name.	*Boiling-Point in ° C.*	*Specific Gravity at 15° C.*	*Constituents (Principal).*
Petrol or Gasoline ..	40°– 90°	0·642–0·648	C_6H_{14}–C_7H_{16}
Naphtha or Ligroin ..	90°–120°	0·648–0·692	C_7H_{16}–C_8H_{18}
Benzine or Benzoline ..	120°–150°	0·692–0·730	C_8H_{18}–C_9H_{20}
Kerosene or Paraffin Oil	150°–300°	0·790–0·810	$C_{10}H_{22}$–$C_{16}H_{34}$
Lubricating Oils ..	—	—	—
Vaseline	—	—	—
Paraffin Wax	—	—	—

The lubricating oils, vaseline, and paraffin wax are obtained from the higher boiling fractions of the petroleum.

From the crude petroleum the following proportions are obtained on an average:

Petrols, Ligroin, and Benzine about	17 per cent.
Kerosene or Paraffin Oil about ..	54 „
Lubricating Oil about	17 „
Vaseline about	variable.
Paraffin Wax about	2 per cent.

Russian petroleum, however, contains a large proportion of hydrocarbons (*i.e.*, substances composed of hydrogen and carbon only) which do not belong to the paraffin or methane series, but to the naphthene series. Their general formula is of the ring type, so that their constitution is more similar to that of the benzene (*not benzine*) derivatives (see p. 192), but their behaviour on combustion is little different from that of the members of the paraffin series.

In organic chemistry there are many series of compounds, such as the methane series typifies. They are called **homologous series.**

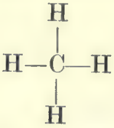
Just as methane, CH_4, is the first member of the methane series, C_nH_{2n+2}, so

Ethylene, C_2H_4, is the first member of the ethylene series, C_nH_{2n}, and

Acetylene, C_2H_2, is the first member of the acetylene series, C_nH_{2n-2}, and

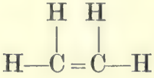
Benzene, C_6H_6, is the first member of the benzene series, C_nH_{2n-6}.

From the above acetylene, C_2H_2, and benzene, C_6H_6, have the same (percentage) compositions, but they are two entirely different substances. This difference is due to the internal arrangement of their constituent atoms—it is due to what is called their constitutions. Such bodies are called **isomeric bodies** or **isomers.** Graphically, the formula for methane, ethylene, acetylene, and benzene are written:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$$

CH_4 methane

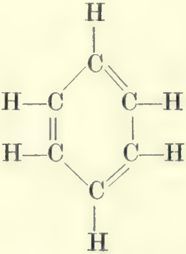


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & = & C & — & H \end{array}$$

C_2H_4 or ethylene

$H—C\equiv C—H.$

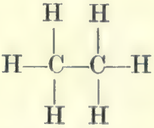
C_2H_2 or acetylene



C_6H_6 or benzene.

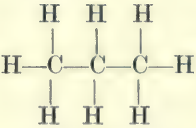
In each case the valencies of carbon, 4, and of hydrogen, 1, are maintained.

Ethane, propane, etc., like methane, have no double bonds:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

C_2H_6 or ethane



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

C_3H_8 or propane

Such substances are said to be **saturated,** whereas ethylene, acetylene, and the like are **unsaturated.**

CHAPTER XIV

Carbon Monoxide, CO.

Molecular weight = 28; density = 14; specific gravity = 0·972. The gas is also known as Whitedamp and as Carbonic Oxide.

Occurrence.—Carbon monoxide occurs wherever there is incomplete combustion of carbon or carbonaceous material. It is produced when carbon dioxide passes through red-hot carbon, and it may be prepared in this way. Carbon monoxide is the gas which is seen burning with a blue flame on top of a coke fire, but its presence there may *not* be due to the carbon dioxide first formed towards the bottom of the fire passing through the red-hot carbon (coke) and being reduced to the monoxide in the process, though the above is the commonly accepted explanation. It is possible that the monoxide is formed before the dioxide, and with the prevailing conditions is the more stable until it meets with sufficient oxygen at the top of the fire to enable it to burn to the dioxide. Carbon monoxide is also formed in the distillation of coal at gas works or coke-oven plant; and it is produced in much greater quantity when steam or air (or both) is blown in at the bottom of the retort. The formation of carbon monoxide by this means is made use of in blast furnaces and in producer-gas, water-gas, and suction-gas plants. Carbon monoxide is also produced in the burning of limestone, where the limestone is mixed with the powdered coal (see p. 131).

In the mine carbon monoxide is formed from gob-fires, from the firing of certain explosives, from coal-dust explosions, and from the slow oxidation of coal.

Preparation.—1. Pass CO_2 over coke or charcoal heated to redness in an iron tube. Bubble the escaping gas through a solution of caustic soda in order to absorb any unchanged carbon dioxide. Collect the gas over water:

$$CO_2 + C = 2CO.$$

2. By the action of sulphuric acid on formic acid:

$$\boxed{H_2SO_4} + \underset{\text{Formic acid}}{H.COOH} = \boxed{H_2SO_4} + H_2O + CO.$$

The sulphuric acid breaks up the formic acid and extracts the elements of water (H_2O), liberating at the same time carbon monoxide.

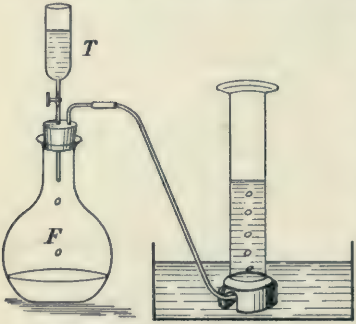


Fig. 87.—Preparation of Carbon Monoxide from Formic Acid.

The apparatus is shown in Fig. 87. A little formic acid is poured into the flask, and the sulphuric acid is run in from the drop funnel *T*. When a few jars of the gas have been collected the gas should be ignited at the end of the delivery tube and allowed to burn as fast as it is formed. (Carbon monoxide is exceptionally poisonous.)

3. By the action of sulphuric acid on oxalic acid. The oxalic acid is decomposed into water, CO_2, and CO.

$$\underset{\text{Oxalic acid}}{\begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array}} \boxed{+ H_2SO_4} = \boxed{H_2SO_4} + H_2O + CO_2 + CO.$$

The sulphuric acid readily absorbs the water. The CO_2 and CO together are then passed through a solution of caustic soda in bottles *DD* (Fig. 88) and over broken sticks of caustic soda in the tower *E*. The CO_2 is thus completely absorbed, and the CO passes on to be collected over water as shown.

Properties.—Carbon monoxide is a colourless, odourless, tasteless gas, very slightly soluble in water. It does not support ordinary combustion, but it burns with a flickering blue flame to form carbon dioxide—

$$2CO + O_2 = 2CO_2.$$

The gas, from its readiness to combine with oxygen, is a powerful reducing agent, oxygen being readily extracted at high temperatures from many metallic compounds. This fact is made use of in the smelting of ores—*e.g.*, iron ores. Carbon monoxide is intensely poisonous, and its physiological effects have been carefully investigated by Dr. Haldane.

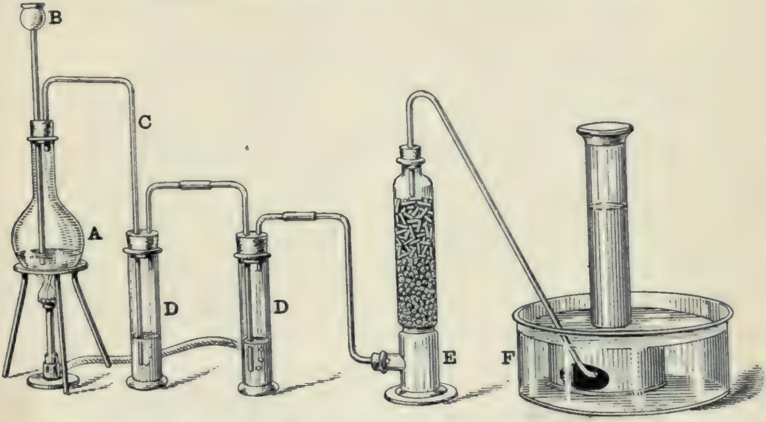


FIG. 88.—PREPARATION OF CARBON MONOXIDE FROM OXALIC ACID.

Physiological Effects. — The hæmoglobin of the blood has a much greater affinity—estimated about 250 to 300 times as great—for carbon monoxide than for oxygen; and with carbon monoxide the hæmoglobin forms a stable pink compound called "carboxyhæmoglobin." This rapidly reduces the oxygen-absorbing power of the blood, and, the body being deprived of oxygen, death ensues. The body of a victim from carbon monoxide poisoning has, in consequence, a ruddy, healthy-looking appearance, which it retains for some time after death.

The intensity of the physiological effects of the gas depends upon the length of time of breathing the noxious atmosphere, the proportion of carbon monoxide present, and the amount of exertion and the physical condition of the individual.

Carbon monoxide is a cumulative poison. On an average the blood of an individual can absorb about 600 c.c. of the gas, when the blood is said to be saturated. If only half this quantity of carbon monoxide is absorbed, the blood is 50 per cent. saturated, and so forth. With various saturations of the blood various effects are produced:—

PER CENT. SATURATION WITH CO.	EFFECT.
Below 20 ..	.. No apparent poisonous symptoms.
20 ..	.. Tendency to giddiness, with headache.
50 ..	.. Weakness of the limbs, mental confusion resulting in hysterics or in drowsiness and stupidity.
Above 50 ..	.. Partial loss of consciousness, especially on exertion.
80 ..	.. Death ensues.

If CO is present in the air to the extent of over 0·25 per cent., the saturation of the blood rapidly increases, especially on exertion, until death ensues. Thus Dr. Haldane has found that when resting and breathing in an atmosphere containing 0·1 per cent. of CO, 20 per cent. saturation was produced in about two hours, and when resting and breathing an atmosphere of 0·2 per cent. CO, 50 per cent. saturation was produced in about one hour. On exertion, the above times are considerably shortened—in fact, they may be halved, an atmosphere containing 0·1 per cent. of CO producing 20 per cent. saturation of the blood in about one hour and an atmosphere containing 0·2 per cent. CO producing 50 per cent. saturation of the blood in about half an hour. For very small amounts of carbon monoxide—less than 0·2 per cent.—the time element is not so important, as a certain percentage saturation is reached after a while, which saturation does not appear to increase. According to Dr. Haldane,* the maximum absorption with—

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* *Methods of Air Analysis*, by J. S. S. Haldane, published by Charles Griffin and Co.

0·02 per cent. CO is 20 per cent. saturation.
0·04 ,, ,, 33 ,, ,,
0·08 ,, ,, 50 ,, ,,
0·16 ,, ,, 66 ,, ,,

With these small percentages it would appear that a kind of equilibrium is set up in the blood between the CO and the O, somewhat similar to the equilibrium which prevails between the CO_2 and the O in the system. The above results are given by Haldane as averages, many of the experiments being performed on himself. The behaviour in individual cases varies considerably, but anything above 0·1 per cent. CO in the air must be considered distinctly dangerous. Recently Haldane has suggested that even smaller quantities may be serious. In his experiments he has found that after inhaling carbon monoxide over long periods his system has become somewhat acclimatised and has tended to adjust itself to the new conditions. It is well to bear in mind that the human system is of a most plastic and adjustable nature if the changes are enforced *gradually*.

Method of Testing for Carbon Monoxide.—The common method at present of testing for this gas is to observe the effect of the suspected atmosphere on some small warm-blooded animal. A mouse or a bird shows symptoms of poisoning before a man does. The exact relation of time cannot be fixed, but it is roughly estimated that a linnet is affected in about one-tenth of the time necessary to affect an average man. Haldane found that when at rest he could breathe for a short time an atmosphere containing 0·4 per cent. CO, while a mouse breathing the same atmosphere showed signs of muscular relaxation in about two minutes and was overcome in four minutes. Birds are more sensitive than mice.

Testing for CO in the Mine.—In the mine, when testing for CO, a mouse or a bird—or both—in cages large enough to permit of free movement are slowly carried into the suspected atmosphere and the effects observed. If the air contains dangerous quantities of CO, the bird soon becomes unsteady on its perch and ultimately falls to the floor of the cage, where it lies resting on its breast, its legs being incapable of supporting the body. In the case of a mouse the effects of CO are indicated by the mouse becoming less lively, losing the power of its legs and " sprawling " on the bottom of the cage.

Precautions.—1. The observer must proceed slowly, otherwise he may travel too far into the poisonous atmosphere to permit of his safe return.

2. Different animals of the same species may be affected differently by the same percentage of CO. Hence, more than one animal should be used at the same time.

3. Men may become affected, especially if excited and/or working vigorously, by the presence of small percentages of CO before the small animals at rest in the cage show any symptoms.

The following tables indicate the effects of various percentages of CO on a linnet and on a mouse:

Per Cent. of CO.	Effect on Linnet.
0·09	Slightly distressed in thirty minutes, and not much further affected after one hour.
0·12	Lost liveliness in fifteen minutes, and thenceforth remained comparatively quiet; did *not* fall off perch in one hour.
0·15	Showed slight distress in three minutes; swayed and fluttered from its perch after eighteen minutes; lost all muscular power and showed symptoms of extreme weakness after one hour.
0·20	Marked distress in one and a half minutes; unsteady in three minutes; fell off perch in five minutes; on exposure to fresh air regained its feet in two minutes and its normal condition in five minutes.
0·29	Fell off perch in two and a half minutes; revived on exposure to air in five minutes.

PER CENT. OF CO.	EFFECT ON MOUSE.
0·16 ..	Became sluggish in six minutes; no further effect after two hours.
0·20 ..	Showed distress in eight minutes; partial collapse in fifteen minutes; died in two hours.
0·31 ..	Showed symptoms in four minutes; partial collapse in seven and a half minutes; lost all muscular power in thirty-five minutes; in fresh air it regained its normal condition in two hours.
0·46 ..	Distinct symptoms in two minutes; partial collapse in four minutes; lost all muscular power in eight minutes.
0·57 ..	Distinct distress in one minute; partial collapse in two minutes; lost all muscular power in seven and a half minutes; and died in sixteen minutes.
0·77 ..	Distinct distress in one minute; lost all muscular power in five and a half minutes; died in twelve and a half minutes.

Estimation of Small Percentages of Carbon Monoxide in the Mine Air.—Due to the extremely poisonous nature of carbon monoxide it is necessary to have some means not only of detecting the presence of traces of the gas, but also of estimating the amount. This is desirable on the grounds that the presence of more than a minute trace of carbon monoxide frequently indicates a gob-fire outbreak. There are two principal methods of estimation:

1. By the effect on the colour of animal **blood solution.**
2. By means of **iodine pentoxide.**

Method 1 is described in detail by Dr. Haldane in his book *Methods of Air Analysis*. There are two methods, one for rough work, the other for more accurate. The principle of the rough method is that a mouse is first allowed to breathe the suspected atmosphere until its blood has reached the maximum saturation with carbon monoxide possible under the circumstances. The mouse is then drowned and a little of its blood taken from the heart and diluted with water. A solution of pure blood from the finger is now made of the same *intensity* as the mouse-blood solution, though the tint may be different. Half of this pure blood solution is saturated with carbon monoxide by bubbling coal gas through it for a few minutes. There are now three solutions. The tint of the mouse-blood solution is a rough guide to the degree of saturation with CO, and therefore to the amount of CO present in the suspected atmosphere. In the more accurate method, however, the amount of CO is found in a different manner—viz., by shaking pure blood solution with a known volume of the suspected air and then titrating with carmine solution (*Methods of Air Analysis*, by J. S. S. Haldane). The titration requires great care, and the method in general is somewhat complicated.

2. The method of estimation by means of **iodine pentoxide** was adopted by Gautier and Clausmann (*Comptes Rendus*, cxxvi., p. 793), but has recently been investigated with special reference to the estimation of CO in mine air by J. Ivor Graham (*Journal of the Society of Chemical Industry*, January 31, 1919, vol. xxxviii., pp. 10-14T.), who has devised a convenient apparatus for the purpose.

The principle of the method lies in the fact that CO reacts with iodine pentoxide, I_2O_5, to form CO_2, and free iodine (I). The reaction is quantitative, so that from the amount of iodine, or of CO_2, formed the amount of CO can easily be calculated. The equation is:

$$5CO + I_2O_5 = 5CO_2 + I_2.$$

The reaction proceeds most readily at temperatures between 100° and 150° C., and it is found more convenient to estimate the iodine than the CO_2. Iodine is a dark violet solid, easily volatilised in air—like camphor or naphthalene—without first turning to a liquid. It is an element and a non-metal. Iodine is soluble in a solution of potassium iodide, KI, which solution is yellow to brown if much free iodine is present. Iodine, *in the free state* and not in chemical combination, reacts with sodium thiosulphate solution quantitatively in the manner indicated by the equation:

$$2Na_2S_2O_3 \quad + \quad I_2 \quad = \quad Na_2S_4O_6 \quad + \quad 2NaI.$$

Sodium thiosulphate+iodine=sodium tetrathionate+sodium iodide

$$2(\overline{23\times2}+\overline{32}\times2+\overline{16\times3}+2(127)=(\overline{23\times2}+\overline{32\times4}+\overline{16\times6}+2(23+127)$$

The free iodine is changed into combined iodine.

Another important property of iodine, made use of in this determination, is the fact that the *slightest trace* of free iodine turns starch solution dark blue. Now if, say, 10 grams of sodium thiosulphate are dissolved in 1,000 c.c. of water, then 1 c.c. of the solution will contain a very small amount—viz., 0·01 gram—of sodium thiosulphate—and 0·1 c.c. will contain 0·001 gram of thiosulphate. It is important to realise how, by means of solutions, the amounts of interacting substances may be made exceptionally small. It is an easy matter to read to 0·1 c.c. on a graduated burette, and the procedure therefore is this: Pass 100 c.c. of the suspected air over hot iodine pentoxide and then through some potassium iodide solution to absorb any iodine vapour formed. Add a few drops of starch solution to the potassium iodide solution. If any CO be present in the suspected air, a blue coloration will be produced. Now run in drop by drop from a burette (see Fig. 91, p. 217) a solution (of suitable and known strength) of sodium thiosulphate, until the blue colour is just dispelled. This indicates that all free iodine has been converted into NaI. Read off the volume of sodium thiosulphate solution used up and estimate the weight of $Na_2S_2O_3$ involved. Then, knowing the weight of $Na_2S_2O_3$, calculate the weight of iodine with which it has acted, remembering that 316 grams of $Na_2S_2O_3$ react with 254 grams of iodine.

Now from the equation—

$$\underset{(5\times28)}{5CO} + I_2O_5 = 5CO_2 + \underset{(2\times127)}{I_2}$$

140 grams of CO yield 254 grams of iodine. It is easy, therefore, to calculate the weight of CO which has produced the above weight of iodine. (The iodine need not be calculated, as it follows from above that 316 grams of $Na_2S_2O_3$ correspond

to 140 grams of CO, but it is well for the student to trace every step.) The volume of CO may then be found by calculation from its density at the temperature of the original 100 c.c. of air, and the volume present expressed as a percentage in the usual manner.

Normally the method yields results accurate to 0·01 per cent. when the CO per cent. is less than 0·2, but see *Note* 2 below.

Note.—1. It is necessary to remove from the air-sample any CO_2 or unsaturated hydrocarbons which may be present *before* passing the air over the I_2O_5 for CO estimation, otherwise inaccurate results are obtained. The CO_2 is removed by bubbling the sample through a solution of caustic soda; and the unsaturated hydrocarbons (such as ethylene) are absorbed by bubbling the sample through a 10 per cent. solution of bromine in potassium bromide solution. Finally, traces of moisture are removed by passing the gas over phosphorus pentoxide.

2. The slightest traces of carbon monoxide may be detected by this method, and the accuracy of the method increased by passing two or three lots of 100 c.c. each of the air over the iodine pentoxide.

Fig. 89 shows diagrammatically the arrangement. (In mine air unsaturated hydrocarbons seldom occur.) A known volume of the suspected air is passed first through a caustic soda tower to absorb any carbon dioxide and then through the U-tube containing the iodine pentoxide, whose temperature is maintained at about 100° C. by means of the heated bath

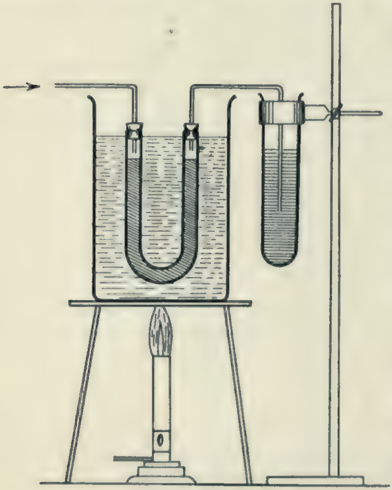


FIG. 89.

of water. The iodine evolved—if any CO is present—passes into the test tube which contains the potassium iodide solution. After the known volume of air has been passed, the test tube is removed and a little starch solution is added. If any blue coloration is obtained, the sodium thiosulphate solution is run in from the burette until the colour just disappears, and the amount of CO calculated, as shown above.

Note.—In the mine a thermos-flask containing hot oil is used in place of the beaker of hot water.

Sulphuretted Hydrogen, H_2S.

Molecular weight = 34; density = 17; specific gravity = 1·18.

This gas is also known as Hydrogen Sulphide and, in the mine, as "Stinkdamp."

Occurrence and Formation.—Sulphuretted hydrogen is liberated during the decay of animal or vegetable matter containing sulphur, the process being due to bacterial action, as in the case of methane formation from cellulose. The action of bacteria on sulphides gives rise to the gas, as also does the action of acids on sulphides. In the distillation of coal at gas-works and coke-oven plant sulphuretted hydrogen is evolved in small amount along with the other gases. In the mine, sulphuretted hydrogen is evolved with carbon monoxide during the heating of the coal associated with underground fires. The gas is also found in certain firedamps, in old goaves or wastes, and especially in stagnant mine water.

Preparation.—Pour cold dilute sulphuric acid on ferrous sulphide, FeS—

$$\underset{\substack{\text{Ferrous}\\\text{sulphide}}}{FeS} + H_2SO_4 = \underset{\substack{\text{Ferrous}\\\text{sulphate}}}{FeSO_4} + H_2S.$$

(Ferrous sulphide may be made as follows: Heat together a mixture of about 2 parts by weight of iron filings and 1 part of sulphur. After heating a while the mixture begins to glow brightly. When the action has finished, allow to cool. Crude ferrous sulphide is left as a cake.)

The apparatus shown on p. 119 for the preparation of hydrogen may be used, substituting ferrous sulphide for zinc.

Properties.—Sulphuretted hydrogen, H_2S, is a colourless gas with the most repulsive smell of rotten eggs. It does not support combustion, but it can be made to burn in air or oxygen. It burns, in these cases, with a bluish flame. With excess of oxygen the above combustion results in the formation of sulphur dioxide, SO_2, and water. With shortage of oxygen, sulphur and water are formed.

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O \text{ (excess of oxygen).}$$
$$2H_2S + O_2 = 2S + 2H_2O \text{ (deficit of oxygen).}$$

The gas is somewhat soluble in water, 1 volume of water dissolving at ordinary temperatures and pressures about 3 volumes of H_2S. The gas is less soluble in warm water, and is therefore often collected over warm water instead of cold.

Sulphuretted hydrogen is intensely poisonous, even more so than carbon monoxide.

Physiological Effects of Mixtures of H_2S and Air.

Per Cent. H_2S.	
0·07	If breathed for a long time may be fatal.
1·00	Causes death in comparatively short time.
3·00	Causes death almost immediately.

As in the case of carbon monoxide, birds or other small warm-blooded animals are more rapidly affected than are human beings.

Tests for Sulphuretted Hydrogen.—1. Its smell of rotten eggs provides good indication of its presence, and it is usually sufficiently unpleasant to cause men in the mine to withdraw from the dangerous area. It is, however, possible after being for some time in an atmosphere containing a little H_2S to become more or less indifferent to—in certain cases rather fond of—the tainted air. This fact accounts, no doubt, for many of the cases of poisoning by the gas, not only in mines, but also in sewers and the like.

2. The action of the gas on lead-acetate papers is a fairly good test—though, under ordinary mine conditions, far from

being as sensitive as the sense of smell. If a piece of filter-paper or white blotting-paper be soaked in lead acetate solution and then, while moist, held in the suspected atmosphere, the paper will be turned first brown and then black if sulphuretted hydrogen be present. The colouring of the paper is due to the formation of lead sulphide, PbS, from the moist lead acetate—

$$\underset{\text{Lead acetate}}{(CH_3.COO)_2Pb} + \underset{\substack{\text{Sulphur-}\\\text{etted}\\\text{hydrogen}}}{H_2S} = \underset{\substack{\text{Lead}\\\text{sulphide}}}{PbS} + \underset{\text{Acetic acid}}{2CH_3.COOH}.$$

The gases given off when coal is distilled are freed from the H_2S which is present by passing the impure coal gas over lime or over iron oxide. These substances react with and consequently absorb sulphuretted hydrogen. The iron oxide is usually in the hydrated state, and the reactions represented by the following equations take place:

$$Fe_2O_3.H_2O + 3H_2S = Fe_2S_3 + 4H_2O$$

and

$$Fe_2O_3.H_2O + 3H_2S = 2FeS + S + 4H_2O.$$

The material (*i.e.*, the spent iron oxide) is revivified by exposing it to the air and allowing to oxidise:

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 3S_2$$
$$12FeS + 9O_2 = 6Fe_2O_3 + 6S_2.$$

Sulphur Dioxide, SO_2.

Molecular weight = 64; density = 32; specific gravity = 2·22.

Occurrence and Formation.—Sulphur dioxide is formed during volcanic action, and in general by the combustion in oxygen or air of sulphur or of substances containing sulphur. It is found in the air of towns derived principally from the combustion of the sulphur contained in coal.

Preparation.—1. The gas may be obtained by burning sulphur in air or oxygen—

$$S + O_2 = SO_2.$$

2. In the laboratory the gas is commonly prepared by heating sulphuric acid with copper—

$$\underset{\text{Copper}}{Cu} + 2H_2SO_4 = \underset{\text{Copper sulphate}}{CuSO_4} + SO_2 + 2H_2O.$$

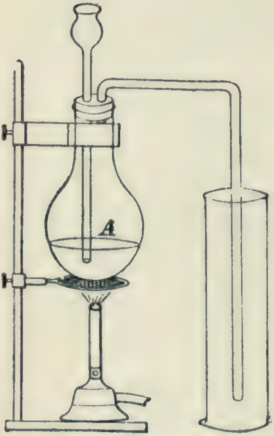


FIG. 90.—PREPARATION OF SULPHUR DIOXIDE.

The SO_2, being a very heavy gas, can easily be collected by displacement of air, as in the case of CO_2 (Fig. 90).

Properties.—Sulphur dioxide (SO_2) is a very heavy colourless gas with a most penetrating and suffocating smell. It is employed for fumigating purposes, and is then usually obtained by burning a piece of sulphur in the room to be fumigated. It will not burn in air, nor will it support ordinary combustion. It is very readily soluble in water, and, if desired pure, it is collected over mercury, on which it has no appreciable action. The solution of SO_2 in water is strongly acid, and is known as sulphurous acid (compare with carbonic acid)—

$$SO_2 + H_2O = H_2SO_3.$$

The sulphurous acid thus formed is gradually oxidised in air to sulphuric acid:

$$\underset{\text{Sulphurous acid}}{2H_2SO_3} + O_2 = \underset{\text{Sulphuric acid}}{2H_2SO_4}.$$

The salts of sulphurous acid are known as sulphites; those of sulphuric acid as sulphates. Thus we have sodium sulphite, Na_2SO_3, and sodium sulphate, Na_2SO_4.

In general, acids containing oxygen in less amount than others, to which they are closely related chemically, have names terminating in *-ous*, and the salts of these acids have names ending in *-ite*. The acids containing the larger amount of oxygen have terminations in *-ic*, and their salts in *-ate*. *E.g.:*

Nitric acid	Sodium nitrate	Nitrous acid	Sodium nitrite
HNO_3	$NaNO_3$	HNO_2	$NaNO_2$.
Chloric acid	Sodium chlorate	Chlorous acid	Sodium chlorite
$HClO_3$	$NaClO_3$	$HClO_2$	$NaClO_2$.

Sulphur dioxide is easily liquefied by pressure at ordinary temperatures (its critical temperature = 157° C.).

The liquid SO_2 is often used as a refrigerating agent.

In the mine SO_2 is rarely met with except in the cases of underground fires, when it may occur in small quantities. At rescue stations, when an irrespirable atmosphere is required, SO_2 is commonly employed, and is produced by burning sulphur in a closed room or gallery.

CHAPTER XV

WATERS.

Surface Waters and Mine Waters.

The chemistry of pure water has been examined in Chapter VII.

There are two distinct types of natural waters:

1. Fresh waters, in which the taste is not appreciably affected by the contained impurities.

2. Mineral waters, which have a distinct taste due to their contained impurities.

Fresh Waters comprise:

(*a*) Rain water, which contains about 0·03 parts of solid matter in 1,000.

(*b*) River and lake waters, which contain about 0·10 parts of solid matter in 1,000.

(*c*) Spring waters, which contain about 0·28 parts of solid matter in 1,000.

(*d*) Deep well waters, which contain about 0·44 parts of solid matter in 1,000.

The above figures are rough averages.

Mineral Waters comprise:

(*a*) Sea or ocean water, which contains about 34 parts of solid matter in 1,000.

(*b*) Inland sea water, which contains varying amounts of solid matter in 1,000. *E.g.:*

Mediterranean Sea, which contains about 40 parts of solid matter in 1,000.

Dead Sea, which contains about 230 parts of solid matter in 1,000.

Elton Lake (Russia), which contains about 270 parts of solid matter in 1,000.

A sample of sea water, on analysis, was found to contain 35·25 parts of solid matter per 1,000 of sample.

The solid matter consisted of:

$NaCl$, sodium chloride	27·06
$MgCl_2$, magnesium chloride	3·67
$MgSO_4$, magnesium sulphate	2·29
$CaSO_4$, calcium sulphate	1·41
KCl, potassium chloride..	0·76
$CaCO_3$, calcium carbonate	0·03
$MgBr_2$, magnesium bromide	0·03
Total =	35·25

The "mineral waters" of Epsom contain as their solid content chiefly magnesium sulphate and magnesium chloride. The "mineral waters" of Harrogate contain chlorides, sulphur, and a trace of sulphuretted hydrogen. Apollinaris, Seltzer, and Idris waters contain carbon dioxide under pressure. When the pressure is reduced the escape of the CO_2 causes the effervescence.

Rain Water is seen to be the purest natural water, but it contains dissolved CO_2 and, near towns and works, sulphuric acid and nitric acid, though the latter is usually combined with ammonia as ammonium nitrate. Rain water consequently has a decided chemical action on rocks, metals, etc., in addition to its erosive or mechanical action. The action on calcareous rocks—*i.e.*, those composed largely of $CaCO_3$, was discussed on p. 160, where it was seen how water containing CO_2 acts as a solvent and dissolves $CaCO_3$ in the form of $Ca(HCO_3)_2$. The sulphuric acid is derived from the burning of matter containing sulphur — coal contains somewhat more than 1 per cent. sulphur on an average. The sulphur first burns to SO_2, which, with the water vapour of the atmosphere, forms H_2SO_3, and this combines with more oxygen to form H_2SO_4.

The nitric acid (HNO_3) present in the atmosphere and contained in rain water—particularly in the first portions of the downpour—is derived from oxides of nitrogen formed by electrical discharges in the atmosphere (*cf.* p. 130). The rain water of towns often contains considerable quantities of free sulphuric acid, and much damage is done to buildings through the chemical action of such acidic rain water on the building stones and mortar.

A good weathering stone is one which is not easily attacked by the above agencies, and one which will stand changes of temperature—even to alternate freezing and thawing—without disintegration. An open texture which allows water to permeate the stone is a great disadvantage as, in such cases, the freezing of the water in the stone results in great stress in the material due to the expansion of water on freezing, and often causes disrupture.

Drinking Waters.—The mineral matter dissolved in natural waters is not usually injurious to health, the injurious property generally consisting in the presence of living germs or bacteria. Contamination with sewage is usually indicated by the presence of ammonia (see p. 136).

Waters safe for drinking comprise spring water, deep-well water, and the water from mountain rivers and mountain lakes.

Waters which are of doubtful degree of purity for drinking comprise stored rain water and surface water, especially surface water from cultivated land.

Waters dangerous to drink comprise river water to which sewage gains access and shallow-well water.

Filtering.—Waters containing solid suspended matter (*i.e.*, not dissolved matter) may be filtered and the suspended matter got rid of by passing the water through filter-beds of gravel, sand, and the like. If the water is intended for drinking purposes, an unglazed earthenware pipe through which the water is forced provides a much more efficient and hygienic filter. When the tube requires cleaning this is best done by first scrubbing and then heating to redness to sterilise it. On cooling it is ready for use again.

Mine Waters.—These vary considerably in their quality, some being so pure as to be quite drinkable, others containing as much as 10 per cent. impurities. The impurities generally found in mine waters consist of:

1. Bicarbonate of calcium, $Ca(HCO_3)_2$.
2. Bicarbonate of magnesium, $Mg(HCO_3)_2$.
3. Sulphate of iron, $FeSO_4$.
4. Sulphate of calcium, $CaSO_4$.
5. Sulphate of magnesium, $MgSO_4$.
6. Sulphuric acid, H_2SO_4.
7. Chloride of sodium, NaCl.
8. Chloride of calcium, $CaCl_2$.
9. Chloride of magnesium, $MgCl_2$.
10. Organic matter.

The presence of the bicarbonates is accounted for by the solvent action of water containing CO_2 on rocks containing $CaCO_3$ or $MgCO_3$. The presence of iron sulphate is due principally to the oxidation of pyrites (FeS_2) in the mine:

$$FeS_2 + 2O_2 = FeSO_4 + S.$$

It will be noticed that free sulphur is formed at the same time, and this may be oxidised to sulphuric acid, giving rise to a particularly corrosive water. The sulphates of calcium and magnesium have as a rule been dissolved by the water in passing downwards through rocks containing these constituents. The coal measures in Britain are often overlain by rocks of Permian and Triassic age, in which the principal deposits of rock salt (sodium chloride) and gypsum (calcium sulphate) are found. Water passing downwards through these rocks may then be expected to contain notable amounts of the above impurities. Indeed, as the Triassic rocks appear to have been laid down largely in inland seas, the salts in the Trias strata are likely to have a close resemblance to those of ordinary sea water. The presence of such substances, therefore, as NaCl, $CaSO_4$, $MgCl_2$, etc., in mine waters is easily accounted for. The organic matter in mine waters is derived from the decay of timber and the decomposition of other organic matter in the mine.

Hardness of Water and Water for Steam-raising Purposes.

The "hardness" of water is a measure of the difficulty with which the water forms a lather with soap. Hardness is due chiefly to the salts of calcium and magnesium; distilled water is soft, and readily gives a good lather with soap.

Soap is essentially a mixture of the sodium salts of certain fatty acids, such as stearic and palmitic acids. Just as common salt or sodium chloride is the sodium salt of hydrochloric acid, so soap is essentially the sodium salt of stearic acid and may be called sodium stearate (but see below). The fatty acids constitute an homologous series of organic compounds:

The first member of the series is formic acid, H.COOH.
The second member of the series is acetic acid, $CH_3.COOH$.
The third member of the series is propionic acid, $C_2H_5.COOH$.
The fourth member of the series is butyric acid, $C_3H_7.COOH$.
The *n*th member of the series is $C_{n-1}H_{2n-1}COOH$.

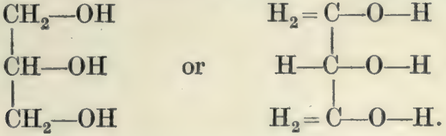
The fatty acids of soap are:

Stearic acid, $C_{17}H_{35}.COOH$, which occurs as a glyceride in mutton fat.
Palmitic acid, $C_{15}H_{31}.COOH$, which occurs as a glyceride in palm oil.
Oleic acid, $C_{17}H_{33}.COOH$, which occurs as a glyceride in olive oil.

Note.—Oleic acid is not a true member of the series.

In soap, these acids are not present as free acids, but as sodium stearate, sodium palmitate, and sodium oleate. Similarly in the fats and oils in which the acids occur, the acids are not in the free state, but combined with glycerine (*i.e.*, glycerol) as glycerine stearate, glycerine palmitate, and glycerine oleate.

Glycerine has the formula $C_3H_5(OH)_3$, or graphically—



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} \quad \text{or} \quad \begin{array}{l} H_2 = C\text{—}O\text{—}H \\ \quad\;\; | \\ H\text{—}C\text{—}O\text{—}H \\ \quad\;\; | \\ H_2 = C\text{—}O\text{—}H. \end{array}$$

Glycerine has the properties of a weak base or alkali. In the manufacture of soap, animal fats are boiled with a solution of caustic soda. Reactions of the following type take place, forming soap and glycerine—

$$\underset{\substack{\text{Stearate of glycerine,}\\ \text{also called ``stearin''}}}{(C_{17}H_{35}.COO)_3.C_3H_5} + \underset{\text{Caustic soda}}{3NaOH} = \underset{\substack{\text{Stearate of sodium}\\ \text{or ``soap''}}}{3C_{17}H_{35}COO.Na} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}.$$

(Observe the replaceable hydrogen of the fatty acids is the one atom of hydrogen contained in the COOH group.)

The soap is separated from the solution by adding brine, which causes the soap to be precipitated. The glycerine is obtained as a by-product. It may be converted into nitroglycerine, the explosive, by treating with a mixture of nitric and sulphuric acids (see p. 225).

Ordinary soap is seen, then, to be a mixture of sodium stearate, sodium palmitate, and sodium oleate. Soft soap is a mixture of potassium stearate, etc., with much glycerine present and free caustic potash. The cleansing action of soap depends upon the fact that the lather formed with water attacks the greasy products of the skin pores, and the chemical and mechanical actions combine in assisting the removal of the dirt. If, however, salts of calcium and magnesium are present in the water used, they react with the soap, forming a "curd" of insoluble stearates, etc., of calcium and magnesium, and a permanent lather cannot be formed until all the calcium and magnesium salts have been converted to insoluble stearates, etc.—

$$\underset{\text{Sodium stearate}}{2C_{17}H_{35}COONa} + \underset{\text{Magnesium sulphate}}{MgSO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Magnesium stearate}}{(C_{17}H_{35}COO)_2Mg}$$

There are two kinds of hardness of water: (1) **Temporary;** and (2) **Permanent.**

Temporary hardness is hardness which is removed by boiling. It is due to the bicarbonates of calcium and magnesium (see p. 160). On boiling, carbon dioxide is given off, and the bicarbonate is changed to the insoluble carbonate which is precipitated—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

If, therefore, such hard water is used (in an untreated condition) for steam-raising purposes, a scale or lining of $CaCO_3$ will form on the interior of the boiler (see below). The furring of kettles on the interior is due principally to the deposition of $CaCO_3$ from the tap water on boiling.

Permanent hardness is hardness due to the other salts of calcium and magnesium—principally the sulphates. It cannot be removed by boiling, but only by special treatment. As a rule, the bulk of the hardness of water is temporary hardness, and not permanent, though individual cases differ considerably.

Reasons for Water-Softening.

The presence of the impurities which make water hard results in a considerable waste of soap when the water is used for washing purposes. When the water is used for steam-raising on an industrial scale, as at collieries, there is often an appreciable deposit formed in the boilers and in the economiser pipes. This deposit or **scale** is a bad conductor of heat and consequently causes enormous heat losses, waste of fuel, and general lowering of the efficiency of the steam-raising plant.

Moreover, the scale has a different coefficient of expansion from that of iron and, as it attaches itself very firmly to the boiler plates, undue stress may be set up with the changes in temperature and consequent expansion and contraction of the metal. The boilers and economisers have therefore to be cleaned out very frequently, and in some cases the chipping necessary to remove the scale damages the boiler materially. There is also to be considered the corrosion due to the chemical action of the impurities in the water on the boiler plates and tubes. Carbon dioxide and oxygen dissolved in the water may attack the iron, converting it to carbonate. This can often be noticed by the brown coloration of the water in the boiler water-gauges. Magnesium chloride at high temperatures and under increased pressure reacts with water to form magnesium hydroxide and hydrochloric acid—

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl.$$

The hydrochloric acid so formed is a further source of chemical action, as it will probably attack the boiler plates.

There is clearly much to be gained by precipitating these impurities from the water and having the water to be used in the boiler as pure as possible. The "softening" of the water consists in precipitating the above impurities and yielding a more or less pure soft water.

Water Softening.—The bicarbonates of calcium and magnesium are converted into insoluble carbonates if the correct amount of lime be added to the water. To get rid of temporary hardness, therefore, the correct amount of lime (or other alkali) is added to the water—

$$Ca(HCO_3)_2 + CaO = 2CaCO_3 + H_2O.$$

Or, expressed slightly differently—

$$\underbrace{CaCO_3 + H_2O + CO_2}_{\text{Calcium bicarbonate}} + CaO = 2CaCO_3 + H_2O.$$

It is clear that the function of the added lime is to neutralise and combine with the CO_2 acidity in the untreated water. (CO_2 in solution is a mild acid.) The lime is usually added as slaked lime—*i.e.*, $CaO + H_2O$ or $Ca(OH)_2$ or, more commonly, as milk of lime. The $CaCO_3$ which is precipitated may be allowed to settle in a reservoir or may be filtered off through a bed of sand or coke.

Sodium carbonate, Na_2CO_3, may also be used for the purpose of softening for temporary hardness. Its action is seen from the equation:

$$Ca(HCO_3)_2 + Na_2CO_3 = \underset{\text{Insoluble}}{CaCO_3} + \underset{\text{Soluble}}{2NaHCO_3}.$$

The sodium bicarbonate formed is soluble, however, and the process leads to the accumulation in the boiler of sodium salts;

and it also causes undue "priming"—*i.e.*, as the sodium bicarbonate, $NaHCO_3$, decomposes when heated in the boiler, liberating CO_2—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Moreover, sodium carbonate is much more expensive than lime.

The best use of sodium carbonate is to soften the water for permanent hardness after the temporary hardness has been removed by lime. The action of sodium carbonate on such substances as calcium sulphate and magnesium sulphate may be seen from the equations:

$$CaSO_4 + Na_2CO_3 = \underset{\text{Insoluble}}{CaCO_3} + \underset{\text{Soluble}}{Na_2SO_4}$$

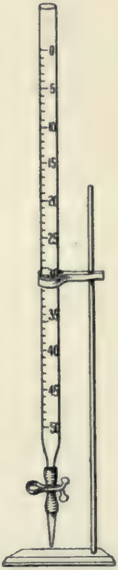
$$MgSO_4 + Na_2CO_3 = \underset{\text{Insoluble}}{MgCO_3} + \underset{\text{Soluble}}{Na_2SO_4}.$$

The $CaCO_3$ and $MgCO_3$ are precipitated from the water before it enters the boiler, but the Na_2SO_4 (sodium sulphate), being soluble, is carried along in solution into the boiler, where it tends to collect. Indeed, the concentration of sodium sulphate in boilers has often reached an almost incredible degree, though by judicious "blowing off" much of the sodium salts which tend to be deposited in boilers may be removed.

Water is sometimes conducted through **peaty ground** before being used in the boiler. This treatment does not prevent scale from forming, but it causes the scale which does form to be more flocculent and not to adhere so firmly to the boiler plates, etc. Such scale is more easily removed than the normal, hard, adherent scale. A similar effect on the scale is produced by adding small amounts of organic substances such as **tannin** and **sodium tannate** to the water. Some organic substances, however, such as cylinder oil (from the water of the condensers) are highly objectionable, as they lead to the formation of a scale which is even a worse conductor of heat than the ordinary scale.

Measurement of the Hardness of Water.—The hardness of water is measured by "degrees." One degree of hardness is represented when there is one grain of calcium carbonate (or bicarbonate equivalent to $CaCO_3$) in 1 gallon of water. Such a water has a certain soap- or lather-destroying capacity, and any other salts in the water which have an equal soap-destroying capacity (see p. 214) are said to produce one degree of hardness.

The hardness of a water may be estimated by means of the following standard soap solution: Dissolve 10 grams of pure Castile soap in 500 c.c. of alcohol and make up the solution to 1,000 c.c. by adding distilled water. 1 c.c. of this solution should raise a *permanent* lather with 70 c.c. of distilled water. To estimate the *total* hardness, take 70 c.c. of the water to be tested in a flask or bottle of about 400 c.c. capacity, and add, from a graduated burette (Fig. 91), the standard soap solution, 1 c.c. at a time, until a *permanent* lather is obtained on shaking vigorously. *The lather should be permanent for at least five minutes.* Then the number of c.c.'s of soap solution less 1 c.c. gives the number of c.c.'s of solution required to soften the water, and the above quantities of soap, etc., are so taken in the standard solution that the number of c.c.'s thus obtained represents the degrees of total hardness of the water. The *permanent* hardness may be found by boiling 200 c.c. of the water for about half an hour in order to precipitate the carbonates, and cooling down the boiled water, taking care to exclude any CO_2. The water is then filtered and any loss in volume made up with boiled distilled water. 70 c.c. of the water thus obtained are taken and the hardness determined by adding soap solution, as above. The number of c.c.'s of soap solution required less 1 c.c. gives the degrees of permanent hardness. The degrees of temporary hardness may be found by subtracting the degrees of permanent hardness from the total hardness.



Burette.

FIG. 91.

Soap has a variable composition and contains much water. The soap solution, after standing for a day or so, should therefore be tested against a standard solution of a calcium salt—usually calcium chloride. The latter solution is made by dissolving 0·200 gram of iceland spar (*i.e.*, pure calcium carbonate, $CaCO_3$) in a little dilute hydrochloric acid and evaporating to dryness. A small quantity of distilled water is then added and the solution again evaporated to dryness, and is repeated a second time in order to get rid of all traces of free hydrochloric acid. The calcium chloride thus formed is then dissolved in distilled water and the solution made up to 1 litre (1,000 c.c.). 70 c.c. of this solution are taken in a flask and the soap solution run in, 1 c.c. at a time, from a graduated burette until a permanent lather is obtained on shaking.

Now 1,000 c.c. of the above calcium chloride solution contains a certain quantity of calcium chloride equivalent in soap-destroying capacity to 0·2 gram of calcium carbonate.

In symbols 1,000 c.c. solution represents 0·2 gram $CaCO_3$. *I.e.*, 1 gallon solution would represent—

$$\frac{0{\cdot}2 \times 4546}{1000} \text{ gram } CaCO_3$$

or

$$\frac{0{\cdot}2 \times 4546 \times 15{\cdot}43}{1000} \textit{ grains } CaCO_3$$

$$= 14{\cdot}0 \text{ grains.}$$

(1 gallon = 4546 c.c.). (1 gram = 15·43 grains).

In other words, the hardness of the calcium chloride solution is 14, and therefore 15 c.c. (14 + 1, see above) of the soap solution should be required to give a permanent lather with 70 c.c. of the standard solution. If, however, 17 c.c. soap solution were required then it is weak, and in calculating hardnesses of water the readings of the burette should be multiplied by a factor—after the subtraction of 1 c.c.—*e.g.*, suppose 70 c.c. of tap water required 10 c.c. of the above (weak) soap solution to yield a permanent lather, then the hardness of the water is $(10 - 1) \times \frac{14}{16} =$ **8 degrees.**

The hardness of water may also be found by titrating with standard acids and alkalies, but this is outside the scope of the present book.

CHAPTER XVI

EXPLOSIVES.

Definition.—An explosive is a substance which can be suddenly decomposed partly or wholly into gases at a high temperature. Explosives are usually solids or liquids, the term "explosives" not being ordinarily applied to gases. The volume of the gases produced by the decomposition or "firing" of an explosive is hundreds of times the volume of the explosive, especially as the gases are at a high temperature at the time of explosion. If there is no ready and spacious outlet for the gases thus generated, enormous pressures may be produced; and this is the property commonly made use of in blasting. The explosion consists as a rule in extremely rapid combustion, the explosive containing in itself the combustible matter and also the oxygen necessary for the process. Some explosives are more sensitive than others; some, such as mercury fulminate, may be exploded readily by slight shock or friction, and these are used as detonators (see p. 235); others, such as tri-nitro-toluene, require a detonator to fire them. The function of a **detonator** is to cause by its own explosion the explosion of a larger mass of less sensitive explosive in which the detonator is imbedded. The detonator is fired either by shock or heat—commonly, in blasting work in coal mines, by means of a metal wire heated to redness, or by a spark from an electric current. The explosion of the detonating substance results in the formation of an explosive wave, which is thought to cause violent vibrations of the molecules of the explosive in contact; and these vibrations cause the latter to decompose and explode. In the firing of explosives of different kinds explosive waves travelling at different rates are formed. Thus dynamite and guncotton yield on firing in an open space a wave travelling about 20,000 feet per second. Ordinary "permitted" explosives used in mining yield waves travelling at about half this rate. Explosives may be classified as (1) low, and (2) high explosives, though this classification is unsatisfactory. Low explosives are explosives which can be fired by ignition—such as gunpowder—whilst high explosives, on the other hand, are not easily fired without detonation. Detonators are usually classed separately. A more convenient classification of explosives is:

1. Mixtures of substances which are individually inexplosive.
2. Explosive *compounds*.
3. Mixtures of explosive and inexplosive substances.

Class 1.—The only important examples of this class are **gunpowder** and **blasting-powder.** They have practically the same composition, and consist of intimate mixtures of potassium nitrate, charcoal, and sulphur. Compositions of various gunpowders are given below:

	British.	*French.*	*German.*	*Blasting-powder (variable).*
Potassium nitrate (KNO_3)	75	72	70	65
Charcoal (C)	15	15	16	15
Sulphur (S)	10	13	14	20

There is usually, also, about 1 per cent. moisture present. Gunpowder is not easily decomposed by shock, and when fired by ignition the rate of explosion is distinctly slow for an explosive. This is due to the fact that gunpowder is a mixture and not simply a chemical compound; and the decomposition which takes place on firing is more or less impeded by having to break up and rearrange a number of different molecules, which are not as intimately linked together as they are in a chemical compound. On explosion gunpowder yields approximately equal weights of solid and gaseous products. The following equation represents the explosion fairly closely:

$$\underset{\substack{\text{Potassium}\\\text{nitrate}}}{16KNO_3} + \underset{\text{Charcoal}}{21C} + \underset{\text{Sulphur}}{5S} = \underset{\substack{\text{Potassium}\\\text{carbonate}}}{5K_2CO_3} + \underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4}$$

$$+ \underset{\substack{\text{Potassium}\\\text{disulphide}}}{2K_2S_2} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{13CO_2} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{3CO} + \underset{\text{Nitrogen}}{8N_2}.$$

1 gram of British Service Powder yields about 265 cubic centimetres of gases measured at N.T.P.

1 ounce of British Service Powder yields about 460 cubic inches of gases measured at N.T.P.

1 pound of British Service Powder yields about 4·26 cubic feet of gases measured at N.T.P.

The above volumes, which have been calculated to N.T.P., would be considerably greater at the temperature of the explosion. From 100 parts by weight of gunpowder the following quantities of gaseous and solid products have been obtained:

Gaseous Products.		*Solid Products.*	
CO_2	22·79	K_2CO_3	19·45
CO	15·22	K_2SO_4	0·28
N	8·58	K_2S_2	17·45
H_2S	3·89	$KCNS$ Potassium sulpho-cyanide	1·39
C_2H_4 (ethylene)	0·70	KNO_3	0·04
H	0·17	$(NH_4)_2CO_3$ Ammonium carbonate	0·84
		S	6·64
		C	0·95
	51·35		47·04

The percentage compositions by volume of the gases formed by explosion of other samples are given below:

	1	2	3 *Blasting-powder.*
CO_2	50·62	51·3	32·15
CO	10·47	3·5	33·75
N	33·20	41·7	19·03
H_2S	2·48	3·5	7·10
CH_4	0·19		2·75
H	2·96		5·22
O	0·08		0·00
	100·00	100·0	100·00

Gunpowder is made in different sizes of pellets for different work. Normally it is a shiny black substance in granular form. Gunpowder as a propellant in the Service has been long discarded in favour of cordite and other nitrocellulose explosives; and in all coal mines in which inflammable gas has been found within the previous three months in dangerous amounts and in all dry and dusty mines the use of gunpowder or blasting-powder is prohibited by law. Indeed, in all such mines no explosive is allowed unless it has passed satisfactorily certain tests and has been placed on the "Permitted List" (see p. 233). The main objections to the use of gunpowder in coal mines consist in (1) the ejection in the form of red-hot or white-hot particles of the solid products left after explosion, these particles being easily capable of igniting any firedamp or cloud of coal dust; (2) the burning of the inflammable gases (*e.g.*, CO) formed on explosion, also liable to cause the above ignitions; (3) the poisonous nature of the gases formed on explosion. Were it not for these serious disadvantages, gunpowder has certain properties which render it superior to any other blasting explosive—particularly for blasting in coal. In the first place, gunpowder does not require a detonator, but can be fired by a squib or fuse. In the second place, the slow nature of the explosion results in a gradual rending action rather than a violent shattering, and therefore yields large pieces of coal with a minimum of "smalls" and dust.

Bobbinite is used only for blasting coal. It must be ignited with a fuse and not with a detonator. There are two types of the explosive, the sulphates of ammonia and copper employed in one being replaced by rice (or maize) starch, and paraffin wax in the other.

Bobbinite (first definition), consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitrate of potassium ..	65·0	62·0
Charcoal	19·5	17·0
Sulphur	2·5	1·5
Sulphate of ammonium Sulphate of copper ..	17·0	13·0
Moisture	2·5	—

the sulphate of ammonia not to exceed 11 per cent. by weight of the finished explosive.

Bobbinite (second definition), consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitrate of potassium ..	66·0	63·0
Charcoal	20·5	18·5
Sulphur	2·5	1·5
Rice or maize starch ..	9·0	7·0
Paraffin wax	3·5	2·5
Moisture	3·0	—

Class 2.—These consist principally of the chemical compounds formed when nitric acid acts on organic substances such as cotton (cellulose) and glycerine, etc.

Guncotton (or nitrocotton or nitrocellulose) is formed when cotton is treated with a mixture of nitric and sulphuric acids. Cotton is fairly pure cellulose. Cellulose $(C_6H_{10}O_5)_x$ or $(C_{12}H_{20}O_{10})_{\frac{x}{2}}$ is the essential constituent of vegetable matter, and is of very complex constitution, the exact number of times the $(C_6H_{10}O_5)$ is contained in the molecule being unknown. In considering the action of nitric acid on the substance the most convenient formula is $C_{12}H_{20}O_{10}$ or

$C_{12}H_{14}O_4(OH)_6$. The action of strong nitric acid may then be represented by the equation:

$$\underset{\text{Cotton or cellulose}}{C_{12}H_{14}O_4(OH)_6} + 6HNO_3 = \underset{\text{Guncotton}}{C_{12}H_{14}O_4(NO_3)_6} + 6H_2O.$$

The guncotton formed is seen to be a cellulose hexanitrate; if less than six (NO_3) groups are present, collodion is formed instead of guncotton. Collodion is the substance from which most celluloids used to be made and from which much of the present-day artificial silk is obtained. The water formed in the above " nitration " is absorbed by the sulphuric acid which is added along with the nitric acid.

The guncotton is, after treatment for twenty minutes to an hour, removed from the acids and washed for several days in water to remove all traces of acidic impurities, otherwise it is not safe in storage.

Guncotton ignites at about 180° C., and if in an open space will burn away rapidly and with a large flame. If, however, the space be small and confined, the combustion is even more rapid; the heat developed is practically all concentrated in heating up the guncotton, and an explosion occurs. The effects of limiting the space so as to hamper the heat and gases in their attempts to dissipate themselves are seen equally well in the detonation of compressed guncotton. In such cases the guncotton explodes violently even though it be unconfined, which explosion is due to the concentration of the heat and gases evolved. Wet guncotton is safe for storing, though it can be detonated by imbedding in it a small piece of dry guncotton and detonating the latter in the usual way.

On explosion guncotton yields the following products, which are all gaseous, there being no solid residue:

	Dry Guncotton.	*Wet Guncotton.*
CO_2	24·24 ..	32·14
CO	40·50 ..	27·12
H	20·20 ..	26·74
N	14·86 ..	14·00
CH_4	0·20 ..	—
	100·00	100·0

The explosion may therefore be approximately represented by the equation—

$$C_{12}H_{14}O_4(NO_3)_6 = 9CO + 3CO_2 + 7H_2O + 3N_2.$$

The steam formed on explosion (temperature about 4,000° C.) oxidises part of the CO to CO_2, leaving free H.

One gram of guncotton yields about 600 c.c. of gases calculated to N.T.P., but the temperature reached on explosion is about 4,000° C., which would make the volume about 9,000 c.c., assuming normal pressure.

In certain mining explosives a little guncotton is often used along with nitroglycerine (see p. 233).

Nitroglycerine or Glycerol-trinitrate, $C_3H_5(NO_3)_3$. Glycerine (or glycerol) as obtained from fats in the manufacture of soap must be purified by distillation, etc., before being used for the manufacture of nitroglycerine. When pure glycerine is treated with a mixture of nitric and sulphuric acids the following reaction occurs:

$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + 3HNO_3 = \underset{\text{Nitroglycerine}}{C_3H_5(NO_3)_3} + 3H_2O.$$

The function of the sulphuric acid is to remove the water as it is formed and also to regulate and slow down the above vigorous reaction. The nitroglycerine forms as an oily liquid on the surface of the mixed acids, and, after standing a while is run off and thoroughly washed with water containing a little soda to remove all acid traces. (Great danger attends the manufacture of nitroglycerine, and many precautions are necessary.)

Properties.—Nitroglycerine is an odourless, colourless, oily liquid of specific gravity 1·6. It solidifies at 4° C. It is insoluble in water. Its ignition-point appears to vary, but it is in the region of 170° C. On complete explosion, nitroglycerine yields all gaseous products in the following proportion, with a certain amount of steam:

$$\begin{aligned} CO_2 &= 63{\cdot}0 \\ O &= 4{\cdot}0 \\ N &= \underline{33{\cdot}0} \\ & \ 100{\cdot}0 \end{aligned}$$

The equation denoting the above changes is:

$$4C_3H_5(NO_3)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2.$$

If, however, the explosion is incomplete, carbon monoxide and nitric oxide, both of which are highly poisonous gases, may be formed in large amount.

Dynamite.—Nitroglycerine is often absorbed in kieselguhr to give the explosive dynamite. Kieselguhr is a porous diatomaceous earth, somewhat similar in general appearance to fuller's earth. Dynamite is not so sensitive to shock as is nitroglycerine; it only contains up to 75 per cent. of the latter, the inert portion being the kieselguhr. Dynamite easily freezes at about 7° C. (or 45° F.), and in the frozen state it cannot be detonated without great difficulty. It is therefore first " thawed " in special pans which consist of zinc water-jacketed cans, the water in the jacket being at a temperature of about 70° C. (or 160° F.). The whole can is surrounded by a layer of non-conducting material such as " felt " in order to prevent loss of heat. It is important thoroughly to thaw the cartridge before use, otherwise a small portion inside may remain after detonation and be a source of danger. Dynamite is not on the " permitted " list, but dynamite, gelignite (see below), and other nitroglycerine explosives are much used in sinking and quarrying (1) because of their violence on explosion, (2) because they are not seriously affected by water, and (3) because the charge necessary occupies a very small space, and therefore only requires a shot-hole of small diameter.

Nitroglycerine may be made into a gelatinous mass by mixing it with guncotton. The mixtures obtained are known as gelignites or blasting gelatines, depending on the proportions present and also on the addition of a small amount of nitrate mixture, etc.

	Blasting Gelatine.	*Gelatine Dynamite or Gelignite.*
Nitroglycerine	93	63·5
Guncotton (*i.e.*, nitro-cellulose)	7	1·5
Sodium nitrate ..	—	27·0
Woodmeal	—	8·0

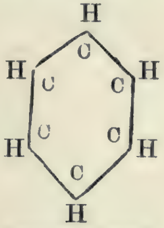
The compositions of gelignites vary considerably; the above contains rather less than the usual amount of nitroglycerine. It is important to note that blasting gelatine and gelignite, unlike dynamite, are very sensitive to shock when frozen (4° C.).

Cordite consists of a mixture of guncotton and nitroglycerine with about 5 per cent. vaseline. The vaseline acts in the double rôle (1) of a lubricant, preventing corrosion and fouling of the lining of guns, and (2) of a stabiliser of the explosive. In the Service cordite is used as a propellant.

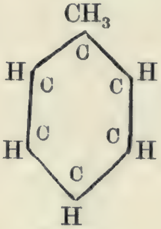
Trinitrotoluene (T.N.T.), etc.—Benzene and toluene are both light, colourless liquids obtained by the distillation of coal at gas works and coke-oven plant. Benzene has the formula C_6H_6, and its molecule is conveniently represented by an hexagonal ring (see p. 192). Benzene is the simplest member or prototype of a vast number of organic compounds known as the "aromatic" compounds.

Toluene has the formula $C_6H_5.CH_3$.

Graphically benzene and toluene are represented:



Benzene or benzol



Toluene

Benzene boils at a temperature of 80° C.
Toluene ,, ,, 110° C.

When benzene is treated with strong nitric acid, mononitrobenzene is formed provided that undue excess of acid is avoided—

$$C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.$$

The presence of sulphuric acid (added to the nitric acid) ensures the removal of the water, which would otherwise hinder the reaction.

Similarly toluene yields on nitration below 35° C. (mono) nitrotoluene—

$$C_6H_5.CH_3 + HNO_3 = C_6H_4(NO_2)CH_3 \times H_2O$$

If, however, excess of acid is employed, di-nitrobenzene and tri-nitrobenzene are formed from benzene; and from toluene are produced by similar treatment di-nitrotoluene and tri-nitrotoluene—

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + 3HNO_3 = \underset{\text{Trinitrotoluene}}{C_6H_2(NO_2)_3.CH_3} + 3H_2O.$$

Trinitrotoluene is a yellow crystalline substance which is not easily exploded except by a detonator. It has largely replaced picric acid (lyddite) in high-explosive shells, as it is safer to handle and is not so likely to decompose on storage. Picric acid tends to attack certain metals (such as lead) to form picrates which are exceptionally sensitive and liable to detonate the explosive on slight shock. Picric Acid or Lyddite, $C_6H_2(NO_2)_3.OH$, is obtained by treating carbolic acid (also known as phenol) with nitric acid—or, in other words, by the nitration of carbolic acid. Phenol, $C_6H_5.OH$, is obtained from coal tar, and with nitric acid under certain conditions the following reaction takes place:

$$C_6H_5OH + 3HNO_3 = C_6H_2(NO_2)_3.OH + 3H_2O.$$

Other similar nitro-compounds of organic bodies are also often employed in explosives. Such are:

Dinitrobenzene, $C_6H_4(NO_2)_2$.
Dinitrotoluene, $C_6H_3.(NO_2)_2.CH_3$.
Trinitronaphthalene, $C_{10}H_5.(NO_2)_3$.

Such nitro-bodies are not necessarily explosive, though they are sufficiently unstable to yield explosive mixtures with ammonium nitrate (see next paragraph).

Ammonium Nitrate, NH_4NO_3 (see p. 142).

When ammonium nitrate is carefully heated, the gas nitrous oxide, N_2O, is produced; but if the heating be vigorous and the ammonium nitrate be dry, an explosion occurs. The explosion may be indicated by the equation:

$$2NH_4NO_3 = 2N_2 + 4H_2O + O_2.$$

Ammonium nitrate is far from being a sensitive explosive, but it is a most valuable substance for mixing with organic nitro-bodies to yield an explosive mixture. If the nitro-bodies (such as nitrobenzene) are not of themselves explosive, the admixture with ammonium nitrate frequently yields an excellent explosive, and such mixtures are known as **Sprengel** or **safety explosives** due to the comparative safety in their manufacture. The nitro-body of itself, however, may be explosive (*e.g.*, trinitrotoluene), and yet admixture with ammonium nitrate may considerably improve the explosive for the purpose required. "Amatol," much used during the late war, is a mixture of ammonium nitrate and trinitrotoluene. Ammonium nitrate leaves no solid residue on explosion, produces no harmful gases, and further, since oxygen is liberated, any incomplete combustion of the organic ingredients of the explosive mixture is assisted towards completion. Thus, any CO may be converted into CO_2.

Mercury Fulminate, $HgC_2N_2O_2$ (see p. 235)

is a highly sensitive explosive used in detonators. Its explosion may be indicated by the equation:

$$HgC_2N_2O_2 = Hg + 2CO + N_2.$$

The volume of CO formed is negligibly small, as only very small quantities of this explosive are employed.

Explosion of Nitro-Compounds.—Practically all of the compounds of class (2) contain as their combustible portion carbon and hydrogen; and much of the oxygen required for the combustion (explosion) is present in the nitro (NO_2) groups. Exactly why these substances should be so violently explosive is not known, but it is probably due to the unstable condition of the (NO_2) groups. Nitrogen in chemical compounds, particularly when in chemical combination with oxygen, often gives rise to instability. In the manufacture of sulphuric acid, the nitric acid fumes (see p. 128) readily part with some of their oxygen and convert the SO_2 to SO_3, which, in the presence of steam, forms H_2SO_4 (sulphuric acid). In the atmosphere the nitrogen is present in the molecular form, N_2, and in such a condition it appears to be particularly inactive, the nitrogen atoms apparently being quite satisfied when they link with one another to form the N_2 molecule. In addition, however, to the nitrogen's unstable nature when in chemical combination, there is produced in explosives by the very disruption of the nitrogen from its combined condition sufficient free " atomic " (and therefore very active) oxygen to ensure the instantaneous combustion of any combustible substances present. In such a body, therefore, as nitroglycerine, $C_3H_5(NO_3)_3$, there are in the molecule 3 atoms of carbon and 5 of hydrogen ready to combine with the 9 atoms of oxygen liberated when the nitrogen breaks away from the combination. The result is that the combustion is instantaneous—or, in other words, the substance " explodes."

Class 3.—In this class are comprised all the **permitted explosives** (see p. 233). They consist of combustible substances (usually explosives of Class 2) mixed with oxidising agents or with some substances which lower the temperature reached on explosion, or with both. The oxidising agents consist of substances which are readily decomposed by heat and liberate oxygen. Such substances include nitrates, such as potassium nitrate, sodium nitrate, barium nitrate, and also chlorates such as potassium chlorate (see p. 156). The bodies used to reduce the temperature reached on explosion include starch, woodmeal, and the like (which, of course, yield practically no solid residue but burn to gases and so give increased pressure); and substances containing much water of crystallisation, such as copper sulphate, $CuSO_4.5H_2O$ and magnesium sulphate, $MgSO_4.7H_2O$. This water of crystallisation is retained by the molecules of the above substances when they crystallise from an aqueous solution; on heating the crystals, though they are quite dry in a physical sense, the water is expelled. In the case of copper sulphate, the blue crystals of $CuSO_4.5H_2O$ are converted to a white powder, $CuSO_4$. Bodies such as ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$, are also used, as they contain water of crystallisation and on decomposition yield only inert gases with no solid matter. Common salt, NaCl, is often incorporated in order that the heat developed may be partly used up in heating and volatilising the salt and thus keep down the temperature; and in some explosive mixtures a little chalk ($CaCO_3$) or other very mild alkali is introduced in order to neutralise any trace of free acid which might cause the explosive to decompose on storage.

About 1 to 6 per cent. of moisture is present as a rule in explosive mixtures of this Class (3). The "permitted" explosives may be conveniently divided into two classes according to whether the principal explosive ingredient is nitroglycerine or ammonium nitrate. Finally, there are mixtures of the two. Nitroglycerine permitted explosives vary considerably in their composition, as may be seen from the following:

Essex Powder consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitroglycerine	24·0	22·0
Nitrocotton	1·5	0·5
Nitrate of potassium	35·0	33·0
Wheat flour (dried at 100° C.)	35·0	32·0
Chloride of ammonium ..	7·0	5·0
Moisture	5·0	2·0

Cambrite (No. 2) consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitroglycerine	24·0	22·0
Nitrate of barium	4·5	3·0
Nitrate of potassium	29·0	26·0
Woodmeal (dried at 100° C.)	35·0	32·0
Carbonate of calcium ..	1·0	—
Chloride of potassium ..	9·0	7·0
Moisture	6·0	3·5

Ammonium nitrate explosives are similarly variable in their compositions, but there is not as a rule as much moisture permissible as in the nitroglycerine type. Also, since ammonium nitrate is hygroscopic, explosives of this class are contained in waterproof cartridge cases. The following are typical:

Ammonite (No. 1) consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitrate of ammonium ..	77·0	73·0
Trinitronaphthalene	6·0	4·0
Chloride of sodium	21·5	19·5
Moisture	1·0	0·0

Roburite (No. 4) consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitrate of ammonium ..	62·5	58·5
Trinitrotoluol	17·5	15·5
Chloride of sodium	24·0	21·0
Moisture	1·5	—

Ammonium nitrate permitted explosives require a stronger detonator; they occupy a larger space, and as a rule they explode with less violence than do the nitroglycerine permitted explosives. Also the products of explosion are harmless gases, principally nitrogen and steam, whereas with the nitroglycerine explosives it is common to obtain carbon monoxide and oxides of nitrogen, which are poisonous gases. Another disadvantage of the nitroglycerine explosives is that nitroglycerine easily freezes (see p. 226).

Of the mixtures of nitroglycerine and ammonium nitrate explosives two examples will suffice:

Super-Excellite (No. 3) consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitroglycerine	10·5	8·50
Nitrocotton	1·0	0·25
Nitrate of ammonium	61·0	57·00
Chloride of sodium	16·0	14·00
Oxalate of ammonium	11·5	9·50
Starch (dried at 100° C.)	5·0	3·00
Castor oil	1·5	0·50
Moisture	2·0	—

Viking Powder (No. 2) consists of the following mixture:

Ingredients.	*Parts by Weight.*	
	Not More Than	*Not Less Than*
Nitroglycerine	9·5	7·5
Nitrate of ammonium	69·0	65·0
Woodmeal (dried at 100° C.)	9·0	7·0
Carbonate of magnesium	1·5	0·5
Chloride of sodium	16·0	14·0
Moisture	2·0	—

These explosives are supposed to combine the advantages of each type, though they also combine the disadvantages. Moisture has to be excluded from the ammonium nitrate, which necessitates a waterproof case for the cartridge, and the freezing of the nitroglycerine may cause further difficulties.

"Permitted" Explosives.—In all dry and dusty mines and in any mines in which inflammable gas has been found within the last three months in such a quantity as to be indicative of danger, no explosive may be employed other than those which have passed the Home Office Test and are on the "Permitted List." The testing station is at Rotherham and the test is carried out as follows: A charge of the explosive, placed in a small cannon without stemming, is fired in a mixture of gas and air. The charge is then increased or decreased until the largest charge which can be so fired without causing ignition of the gas is obtained; and in order to be certain of this five consecutive shots are fired of the same charge, and, if ignition is effected, the above maximum charge is reduced in order to obtain *non*-ignition. The next procedure is to fire shots into mixtures of coal dust and air until the *safe* maximum charge is obtained, as in the case of gas and air—*i.e.*, the charge which will not cause ignition. Whichever of these two safe maximum charges is the lower is known as the **Maximum Charge.** The coal dust employed is ground so that at least 90 per cent. passes a sieve of 150 meshes to the linear inch. The gallery in which the testing is done is about 5 feet in diameter and 30 feet long.

In addition to the above, there is a pendulum test. Shots are fired at the ballistic pendulum in order to compare the "strength" of the explosive and its general behaviour. The ballistic pendulum is a 5-ton mortar swung by 9-foot rods from a horizontal shaft supported in practically frictionless bearings. A shot fired from the cannon causes a certain swing of the pendulum, which swing is registered on a scale. The average swing thus obtained is compared with the swing registered by an equal weight of "gelignite," containing 60 per cent. of nitroglycerine. An explosive passes the tests and is placed on the "permitted" list if—

1. The maximum charge is not less than 8 ounces.
2. No appreciable amount of the charge is left unexploded in the shots of the pendulum test.
3. The explosive has, in the opinion of the officer in charge of the testing, exploded in a satisfactory manner when fired untamped in the gallery.

Various Home Office Regulations which cannot be considered here govern the storage and use of explosives at coal mines.

Detonators (see pp. 219 and 229).—Certain types of detonator may be fired by a time-fuse in naked-light mines, but as these detonators only differ from the others in having no electric wires, it will be sufficient to describe the ordinary type.

The common type of detonator fired by electricity consists essentially of a small copper or tin case about 2 inches long and $\frac{1}{4}$ inch diameter. At one end is enclosed some exceptionally sensitive explosive, and next to this is a priming charge of some easily ignited mixture into which the wires for the electric current are led through the other end of the case. The sensitive explosive commonly employed is fulminate of mercury ($HgC_2N_2O_2$), usually mixed with potassium chlorate ($KClO_3$) in the proportion of 4 parts of fulminate to 1 of chlorate.

Fulminate of mercury is prepared by dissolving mercury in nitric acid and then adding the solution to alcohol. It is obtained as a grey crystalline powder which, when dry, explodes on the slightest friction or on warming to 190° C. (374° F.). The greatest care is therefore necessary in handling detonators. There are two types of detonators—the low-tension and the high-tension. In the low-tension detonators the wires are joined by a fine wire of iron or platinum in the priming charge. When the current is passed from the magneto the fine wire is heated to redness. This ignites the priming charge, which, in turn, fires the fulminate, and this causes the explosion of the cartridge of explosive with which it is in contact. In the high-tension detonators the wires in the priming charge are not joined, the ignition of the priming charge being effected by the spark which jumps the gap when the current is switched on. The fulminate and the cartridge of explosive are fired automatically, as above. Low-tension detonators can be tested before use (care is necessary) by means of a cell and a galvanometer, whereas high-tension detonators cannot, but high-tension detonators are usually preferred on account of their being cheaper and requiring but a small diameter of the firing cable, which may be of considerable length. The insulation, however, needs to be sounder than in the case of low-tension cables. The strength of the detonator to be used is specified in the C.M.A. Regulations, No. 6 or No. 7 detonators being commonly recommended.

No. 6 detonator contains 15 grains of the above fulminate and chlorate mixture.

No. 7 detonator contains 23 grains of the above fulminate and chlorate mixture.

CHAPTER XVII

COAL.

Origin and Formation.—Coal is the " mummified " remains of ancient vegetation which flourished ages ago. The vegetation decayed to varying degrees, was arrested at different stages by the prevailing conditions, and finally preserved by overlying sediments. The nature of the vegetation and the extent of the decay before submergence were probably the governing factors in deciding the type and characteristics of the coals now found. The climate at the time is thought to have been tropical or subtropical, the ground swampy with luxuriant plant growth, and the general conditions similar to those which now prevail on the upper reaches of the Amazon.

The principal constituent of wood fibre is cellulose $[(C_6H_{10}O_5)_n]$, and it is therefore to be expected that coal, which is more or less altered wood, should resemble in some degree the cellulose from which it is derived. In vegetable matter, however, there are also present resins, proteids, sap juices, and a small amount of mineral matter (ash); and coal, therefore, also contains the products resulting from their decay. The cellulose in decaying—the process is bacterial—gives rise to methane (see p. 177) and carbon dioxide, and also to complex organic acids known as humic and ulmic acids, which are found largely in peat bogs. Various other degradation products of cellulose are also formed and are thought to make up an important part of the coal substance. The resinic matter resists decay more than does the cellulose, and is consequently present (more or less altered) in coal to a greater extent than might be expected. The sap juices and proteids undergo decay more readily than either the cellulose or the resins, and as they are not present to a very great extent in vegetation, the residue present in the coal is even smaller. The nucleus and protoplasm of the plant cells consist essentially of proteids. Proteids are organic substances which are composed of about 53 per cent. carbon, 7 per cent. hydrogen, 21 per cent. oxygen, 17 per cent. nitrogen, and 1·5 per cent. sulphur. As coal contains only about 1 per cent. nitrogen derived from the above source, the amount of proteid residues in coal is probably very limited. The " organic " sulphur of the coal (see p. 247) may also be traced to the above source.

The mineral matter or ash is composed of (*a*) the mineral matter or ash of the original vegetation and (*b*) any other mineral matter carried to the coal and deposited there by aqueous solutions circulating either contemporaneously in the decaying vegetation or subsequently from the strata above. Such mineral matter, if more or less completely intermingled with the coal substance, may be fairly termed the ash or mineral matter of the coal, but not otherwise.

It is thought that coal seams represent only about one-fifth of the original weight of the vegetable matter, and only about one-tenth of the original volume.

AVERAGE COMPOSITIONS OF WOOD, PEAT, AND COALS.

Figures are expressed on ash-free basis of the dry material.

Substance.	% *C.*	% *H.*	% *O.*	% *N.*	*Calorific Value.*	
					Cals. per Gm.	*B.T.U. per Lb.*
Wood	50·0	6·0	43·5	0·5	4,000	7,200
Peat	57·0	5·7	35·3	2·0	5,500	9,900
Lignite	67·0	5·0	26·5	1·5	6,500	11,700
Bituminous coal . .	83·0	5·0	10·0	1·0	8,500	15,300
Anthracite . .	93·0	3·0	3·0	0·7	8,500	15,300

The above are only average values. It should be noted that the carbon percentage rapidly increases from wood to anthracite; that at the same time the oxygen percentage rapidly decreases, while the hydrogen percentage changes much more gradually from 6·0 to 3·0.

***Total Analysis of the Organic Portion of a Fuel, etc.**—The above values for carbon and hydrogen are determined by somewhat lengthy analyses which require great care. The principle of the analyses consists in burning about 1 gram of the fuel in a current of dry oxygen and so converting all the carbon to carbon dioxide and the hydrogen to water. The water formed is the first to be absorbed. This is done by passing the products of the combustion through a weighed U-tube full of calcium chloride ($CaCl_2$), which is very hygroscopic, the increase in weight after the experiment being the weight of the water formed. The carbon dioxide is in the vapours escaping from the above calcium chloride tube, and these gases are consequently bubbled through a vessel half full of caustic soda solution ($NaOH$) and previously weighed. The increase in weight at the end of the experiment is the weight of carbon dioxide formed. The amounts of hydrogen and of carbon are calculated from the above weights of water and carbon dioxide, water containing approximately $\frac{1}{9}$ of its weight of hydrogen, and carbon dioxide containing $\frac{12}{44}$ of its weight of carbon.

The **nitrogen** is usually estimated by first converting it to ammonia, as in Kjeldahl's method, which is described in any standard textbook on Practical Organic Chemistry, the amount of ammonia being found by titrating with standard acid. Ammonia contains $\frac{14}{17}$ of its weight of nitrogen.

The **oxygen** is found by difference.

For commercial and industrial purposes the above analyses are seldom required, as much better indications of the nature and suitability of the coal may be obtained from the Proximate Analysis (see p. 242). Even for classification purposes the Volatile Matter Test (p. 246) is most useful, as will be seen from the following table, which is compiled essentially from the original **Regnault-Grüner Classification of Coals** now generally adopted in France and Britain.

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* For exact details the student is referred to any good textbook on Organic Chemistry—*e.g.*, Cohen's *Practical Organic Chemistry*, published by Macmillan. Great care is necessary in performing the experiment.

CLASSIFICATION OF BRITISH COALS.

Class.		*Uses.*	*Percentages on the Dry Ashless Fuel.*					*Nature of Coke.*
			Volatile Matter.	*Fixed Carbon.*	*Total C.*	*Total H.*	*Total $O+N+S$*	
Bituminous coals	1	Long-flame reverberatory furnace coals	40–45	55–60	75–80	4·5–5·7	15–20	Non-coherent loose
	2	Gas coals	32–40	60–68	80–85	5–5·7	10–15	Very open coke
	3	Coking coals	26–32	68–74	85–89	5–5·7	5–11	Good coke
	4	Coking coals and steam coals	18–26	74–82	88–90	4·5–5·5	5–7	Good coke dense
	5	Best steam coal	15–20	80–85	90–92	4·0–4·5	4–6	Poor weak coke
Anthracitic coals and Anthracites		Steam coals	8–15	85–92	92–94	3–4	3–5	No coke
		Stoves and suction-gas plants	<8	>92	„	„	„	„ „

The above classification is very general Certain coals could be fairly placed in more than one section, and others could with difficulty be included in any, *e.g.*, cannels.

Lignites or Brown Coals contain more than 45 per cent. volatile matter (on dry ash-free basis), and would consequently occupy a place in the above table preceding Class 1 of the Bituminous Coals. They occur largely on the Continent in Germany and Austria. In the British Isles they have been worked only in a few places, such as at Bovey Tracey in Devonshire. They vary in their appearance from brown material in which the woody structure is apparent to black solid material having an irregular conchoidal fracture. The great drawback to their economic use is their large water content. Some lignites contain up to 50 per cent. of moisture, which is not easily driven off by air-drying; and, moreover, when they *are* dried, they frequently crumble to a powder which has to be compressed into briquettes to render it saleable as a fuel. However, the economic utilisation of lignites is not confined wholly to their direct use as a fuel, as their distillation yields a large amount of volatile matter, from which are obtained valuable oils such as petrols, paraffin oil, fuel oils, and lubricating oils. Pitch, paraffin wax, and ammonia are also obtained in considerable amount.

The **Bituminous Coals** comprise the vast majority of British coals, and their uses are indicated by the names appended in the table. Long flame coals burn with a luminous, smoky flame, and are sometimes used as house coals, as they are easily ignited. Gas coals are typical "caking" coals—*i.e.*, when heated they swell into a pasty mass which emits blowers of gas. They also make good house coals. Coking coals (having between 20 and 33 per cent. volatile matter at 900° C.) are found in most of the coalfields, but more especially in Durham, Yorkshire, and South Wales. They are not very suitable for steam-raising because of their tendency to coke while burning, and this checks the flow of air through the firebars. The best steam coals contain from 15 to 20 per cent. volatile matter at 900° C. They do not coke to any appreciable extent, require a good draught, and burn with a short flame. They have a higher calorific value than coals of any other class.

Anthracitic coals are in the intermediate stage between Bituminous Coals and true Anthracite. **Anthracite** itself is frequently Bituminous Coal changed or metamorphosed by the pressure and heat developed by earth movements; though certain formations of anthracite are not easily explained in this way. Anthracites have a pitch-like appearance, though they are not soft. They are used for domestic central-heating plants; also in suction-gas plants, and in general whenever a smokeless fuel is required. Anthracites are difficult to ignite; they have a fairly high calorific value, but they excel principally in having a high calorific intensity—*i.e.*, under the proper conditions a very high local temperature may be obtained on their combustion. This is due to their low hydrogen and low volatile matter content and the small amount of ash.

Cannel Coals.—In the foregoing classification cannel coals have been omitted as there is nowadays a tendency to regard them as highly impregnated oil shales, and their origin is doubtful. It has been suggested by some that cannels are the fossil remains of the slime (sapropel) of the shallow lagoons in which the original vegetation of the coal measures flourished, but others account for their origin in different ways. Cannels are generally dull black in colour, fairly easily polished and carved, and break with a conchoidal fracture. On heating in a closed vessel they yield an exceptionally large amount of volatile matter (about 50 per cent.). Cannels have frequently a low ignition temperature, and a piece of cannel, lighted from a match, will burn with a candle-like flame, hence the name "cannel." The cannel coals which contain the most volatile matter yield as a rule a pale brown streak on hard white surfaces. The ash content varies considerably and is usually high (up to 50 per cent.), though some of the famous Wigan cannels have as little as 1 per cent. ash. The high ash content has hitherto been a serious impediment to the commercial utilisation of cannels, but low-temperature distillation may prove that there is a future for the large quantities of inferior cannels which have been so far neglected. Cannels as a rule occur as part of or immediately above or below bituminous coal seams, and many of the poorer varieties which could easily be worked at the same time as the true coal seam are left underground in the "waste," where their spontaneous combustion is a source of danger.

PROXIMATE ANALYSIS OF COAL.

Sampling.—Every care should be taken to obtain a truly representative sample. No general rules can be laid down as different methods have to be adopted in different cases, but the following may be useful: In sampling from a seam in the mine, choose a smooth part of the face and mark on with chalk two vertical lines about 2 feet apart. Clean up the floor and on it lay a clean piece of stout canvas. Now trim out to the full section of the seam that portion between the two marks to a depth of 1 foot or so into the solid coal. Reject any "dirt" not usually filled in, and then break up the sample on the canvas to the size of about 1-inch cubes. Mix thoroughly, make into a pile, divide into four, and reject opposite quarters. Mix the remaining quarters again into a pile, divide into four, and reject opposite quarters as before.

Continue the process until a sample of reasonable bulk—say 20 pounds—is obtained. Unless it is desired merely to sample the seam at this particular spot, the same process is carried out over various lengths of face (say 100 yards), the final samples being mixed together and "quartered," as above, if a single representative sample is required.

In sampling from the surface consignments, the discretion of the sampler should be exercised with every possible care, and large samples should be taken in the first instance. The above process of quartering may have to be employed some dozens of times in sampling large consignments, even though the samples be taken at intervals from the waggons when unloading. Too much stress cannot be laid on the necessity for true and careful sampling, as it is obviously useless making an analysis on part of the material which is not truly representative of the whole.

Physical Examination.—1. Note should first be made of the general appearance of the sample; whether much pyrites is visible; whether much shale or other foreign matter is present; and so forth.

2. **Specific Gravity.**—(*a*) This may be determined on several pieces of the coal (about 1-inch cube) by Archimedes' Principle (see p. 9). The average of the results is recorded as the specific gravity of the sample.

(*b*) The specific gravity may also be determined by means of the specific gravity bottle (see p. 12). The coal for this purpose should not be ground too small—not smaller than rice—or difficulty will be experienced in "wetting" it.

(*c*) A concentrated solution of calcium chloride in water may be prepared on which pieces of the coal will float. Water is now added gradually and the solution stirred until the coal does not float entirely on the top, but remains suspended at any position in the liquid. The specific gravity of the liquid is then taken by means of an hydrometer. This value is the specific gravity of the coal.

The specific gravity of bituminous coals lies as a rule between 1·25 and 1·35.

Chemical Examination.—The sample is broken up into pieces about the size of peas, and "quartered" down to a bulk of 1 pound or so; ¼ pound of this is taken and ground (in a coffee-mill grinder) to a fine powder capable of passing a 150-mesh sieve. All the following determinations are carried out on this finely ground coal: The moisture is determined on the coarser sample also, and the figure obtained is recorded as the true moisture; but it is necessary also to estimate the moisture on the fine sample in order that the results of the other determinations—*e.g.*, ash, coke, etc.—may be expressed on the dry coal. There is as a rule only a slight difference between the moisture of the finely ground coal and that of the coarsely broken material, due to loss in grinding.

1. **Moisture.**—(*a*) About 10 grams of the coarsely broken coal are weighed on to a weighed watchglass, and placed in the water-oven (approximately 212° F.) for one hour. The water-oven is essentially a double-walled copper box with a jacket in which water is maintained boiling by means of a bunsen flame below (see Fig. 82, p. 172). After one hour the glass and contents are removed, allowed to cool in the desiccator, and weighed. [The desiccator (Fig. 92) is a strong glass vessel in the lower part of which is placed some concentrated sulphuric acid in order to maintain a dry atmosphere inside. The sulphuric acid is separated from any material placed inside the desiccator by means of a porcelain partition or a zinc gauze.] The watchglass and coal are now returned to the water-oven for twenty minutes, after which they are removed, allowed to cool in the desiccator, and weighed again. The above process is continued until no further loss in weight is obtained. *E.g.:*

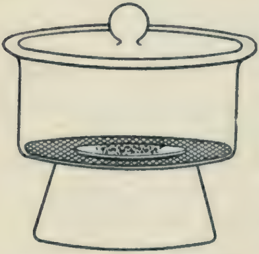

Fig. 92.—Desiccator.

Weight of glass .. = 15·013 grams.
,, ,, and coal = 25·106 ,,
∴ ,, coal .. = 10·093 ,,

Weight of glass and coal:

After one hour in water-oven .. = 24·803
After twenty minutes more in water-oven = 24·782
" " " " " = 24·785

(The gain in weight is due to oxidation.)

$$\text{Then loss in weight} = \text{moisture} = 25{\cdot}106 - 24{\cdot}782 = 0{\cdot}324 \text{ gram.}$$

$$\text{Percentage moisture} = \frac{0{\cdot}324}{10{\cdot}093} \times 100 = \mathbf{3{\cdot}2 \text{ per cent.}}$$

(*b*) About 5 grams of the finely powdered coal are treated similarly. Suppose the moisture on this part of the sample to be 3·0 per cent., indicating a loss of 0·2 per cent. in the grinding. The results obtained for any estimations carried out on this finely ground sample must be multiplied by $\frac{100}{97}$ in order to express them on the dry coal.

2. **Ash.**—About 2 grams of the finely powdered coal are weighed into a wide, shallow, weighed crucible or dish (of porcelain or platinum) and ignited to constant weight either over a bunsen burner or in a furnace to which air can gain easy access. A lid for the crucible or dish must not be used—except for the first minute or so, to prevent loss of solid particles—as it is essential to burn off all the organic matter, and to do this free access of the oxygen of the air is absolutely essential. The process of "ashing" may be assisted by periodically stirring with a platinum wire, but care must be taken to avoid loss. When all carbonaceous matter has apparently burned away—it may take more than one hour—the crucible and contents are allowed to cool in the desiccator and weighed. The crucible and contents are then returned to the burner or furnace and ignited as before for another twenty minutes, allowed to cool in the desiccator and weighed, the process being continued until a constant weight is obtained. *E.g.:*

Weight of crucible .. = 12·438 grams.
" " and coal = 14·539 "
∴ " coal .. = 2·101 "

Weight of crucible and ash:

After one hour .. .. .. = 12·554 grams.
After a further twenty minutes = 12·548 ,,
,, ,, ,, ,, = 12·548 ,,

Then weight of ash = 12·548 − 12·438 = 0·110 gram.

$$\text{Percentage of ash } \textit{on dry coal} = \frac{0{\cdot}110}{2{\cdot}101} \times 100 \times \frac{100}{97}$$
$$= \mathbf{5{\cdot}4\ per\ cent.}$$

3. **Coke, Volatile Matter, and Fixed Carbon.**—(*a*) Weigh about one gram of the finely powdered coal into a weighed platinum crucible (about $1\frac{1}{4}$ inches tall × $\frac{3}{4}$-inch diameter) and cover the crucible with a good-fitting lid. Place over the full flame of a large bunsen burner for seven minutes. Allow to cool in desiccator, and weigh. This is the weight of the crucible and coke. The loss in weight is the weight of the volatile matter and moisture. The fixed carbon is the carbon of the coke, and is found by subtracting the percentage ash from the percentage coke.

(The volatile matter driven off escapes at the top of the crucible round the edges and burns there.)

Weight of platinum crucible and lid = 21·368 grams.
,, ,, ,, ,, and coal = 22·478 ,,
∴ ,, coal = 1·110 ,,

Weight of platinum crucible and lid and coke = 22·088 grams.
∴ ,, coke (22·088 − 21·368) = 0·720 gram.

$$\text{Per cent. coke } \textit{on dry coal} = \frac{0{\cdot}720}{1{\cdot}110} \times \frac{100}{97} = \mathbf{66{\cdot}9\ per\ cent.}$$

$$\therefore \text{ Volatile matter} = 100 - 66{\cdot}9 = \mathbf{33{\cdot}1\ per\ cent.}$$
$$\text{Fixed carbon} = (66{\cdot}9 - 5{\cdot}4) = \mathbf{61{\cdot}5\ per\ cent.}$$

(*b*) The above test may also be checked by igniting 20 to 30 grams of the coarsely broken coal in a fire-clay crucible (covered with the lid) in a muffle furnace or in an ordinary coke fire for about forty minutes, or fifteen minutes after the volatile matter has apparently ceased coming off. By this means a better idea can be formed of the nature of the coke that will be yielded on a large scale. *E.g.:*

Weight of (coarsely broken) coal = 25·00 grams.
,, coke = 16·25 ,,

$$\text{Per cent. coke on dry coal} = \frac{16{\cdot}25}{25{\cdot}00} \times \frac{100}{96{\cdot}8} = \mathbf{67{\cdot}1\ per\ cent.}$$

The coke should be examined for strength, toughness, and general appearance.

Sulphur.—There is usually between 0·5 and 3·0 per cent. sulphur in coal, anthracites as a rule containing less than bituminous coals.

Sulphur in coal is objectionable as, on burning, it yields corrosive sulphurous fumes; produces, if the coal is coked, an unsuitable coke for metallurgical purposes; and, if present as pyrites, gives rise to much clinker in the ash.

Sulphur in coal may occur in four forms:

(1) As sulphur of iron pyrites (or brasses), FeS_2.
(2) As sulphur of the organic coal substance.
(3) As sulphur of sulphates, such as $CaSO_4$.
(4) As free sulphur.

(1) and (2) are the principal sources of the sulphur in coal, but it is customary not to distinguish between any of these in the commercial tests and merely to estimate the total sulphur present in the coal. This estimation may be done in a number of different ways. In most cases, however, the principle of the method is to convert all the sulphur of the coal to sulphates by heating the coal with such substances as sodium carbonate, lime, magnesia, sodium peroxide, etc.

(*a*) One method is as follows: Make up a mixture of 2 parts of magnesia (MgO) with 1 part of sodium carbonate (Na_2CO_3). This is known as Eschka's mixture. Take 1·00 gram of the finely powdered coal in a platinum crucible and mix with 1·0 gram of Eschka's mixture, and finally cover the whole with an additional 1·0 gram of Eschka's mixture. Place the lid on the crucible and heat gently for some time, taking care to avoid the production of smoke from the coal. Gradually heat the crucible more strongly, and finally dispense with the lid and heat to redness until all black specks of carbonaceous matter have disappeared. Allow to cool and then transfer to a beaker, add 10 c.c. of bromine water and boil with about 100 c.c. of (distilled) water. (The object of adding the bromine is to convert any sulphite to sulphate: $MgSO_3 + Br_2 + H_2O = MgSO_4 + 2HBr$.) Filter and wash out the beaker and crucible several times with hot water, pouring the washings through the filter. The insoluble material on the paper may now be discarded. The clear filtrate is acidified with hydrochloric acid, a little ammonium chloride is added (to ensure a granular precipitate) and the liquid boiled until the bromine has been driven off. A slight excess of hot barium chloride solution is now cautiously added and the boiling continued for half an hour. All the sulphur is thus precipitated as white insoluble barium sulphate.

$$MgSO_4 + BaCl_2 = BaSO_4 + MgCl_2.$$

The precipitate is allowed to settle for some hours, and then filtered off on a filter paper, washed thoroughly with hot water and ignited in a weighed platinum crucible, and finally weighed. The filter paper, being completely combustible and yielding only a negligible trace of ash, there is left in the crucible only the unchanged barium sulphate.

	Grams.
Let the weight of the platinum crucible be	= 20·1344
And the weight of the platinum crucible + $BaSO_4$	= 20·2144
Then weight of $BaSO_4$	= 0·0800

And the percentage sulphur in the coal

$$= \frac{0·0800 \times 0·1374 \times 100}{1}$$

$$= 1·10$$

On the dry coal $= \frac{1·10 \times 100}{97} =$ **1·13 per cent.**

Note.—$BaSO_4$ contains 0·1374 of its weight of sulphur.

A "blank" experiment on 2 grams of Eschka's mixture should be done alongside and the sulphur, if any, estimated as above. The difference between the total amounts of sulphur found and the sulphur found in the blank corresponds to the amount of sulphur in the coal. The sulphur in coke may be estimated similarly.

(*b*) A more efficient and reliable method of estimating the sulphur in a fuel is by means of the bomb calorimeter. One gram of the finely powdered coal pressed into a briquette is employed, and a few c.c. of water are placed in the bomb. The bomb is charged with oxygen under a pressure of about 20 atmospheres and the fuel fired by the electric ignition as usual. The sulphur burns to sulphur trioxide, which is absorbed readily by the water in the bomb, yielding sulphuric acid:

$$H_2O + SO_3 = H_2SO_4.$$

The bomb is allowed to stand for fifteen minutes after firing, and the gases formed by the combustion are then slowly bubbled through a dilute solution of caustic soda (free from sulphur). The object is to absorb any sulphurous vapours which may not already have been absorbed by the water in the bomb. A few c.c. of bromine water are added to the caustic soda solution, which is then boiled and acidified with hydrochloric acid. The bomb itself is washed out three times with distilled water, and the washings added to the above solution, which is boiled until free from bromine. Hot barium chloride solution is then added until in excess, the boiling continued for half an hour, and the precipitated barium sulphate allowed to settle out over a few hours. The liquid is then filtered, the precipitate washed thoroughly with hot water, ignited, and weighed. As before, the sulphur is found by multiplying the weight of barium sulphate by 0·1374.

Calorific Value of Coal and Coke.—The principle of the various types of calorimeter employed for this purpose is that the heat produced by the combustion of a certain mass of the fuel is transferred to a known mass of water whose initial and final temperatures are noted. The rise in temperature, however, is undergone not only by the water, but also by the apparatus immersed in the water and the calorimeter vessel holding it. Allowance must clearly be made for this by first employing a fuel of known calorific value, and calculating how many grams of water the apparatus is equivalent to in heat units (calories). This is known as the "water-equivalent" of the calorimeter and may be found as follows:

E.g.: 1 gram of coal of calorific value 8,600 calories per gram raised the temperature from 15·00° C. to 18·00° C.; 2,500 grams of water were used in the calorimeter vessel. What is the water-equivalent?

$$\text{Heat given out} = \text{heat taken in}$$
$$8600 = (2500 + x) \times 3{\cdot}00$$

x being the water-equivalent of the calorimeter and 3·00° C. being the rise in temperature.

I.e., $8600 = 7500 + 3x.$

Whence $x = \frac{1100}{3} =$ **367 grams (water).**

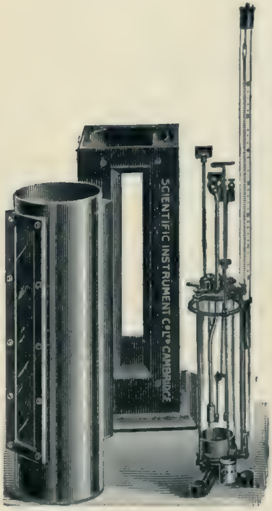

FIG. 93.—ROSENHAIN CALORIMETER.

It is not proposed here to describe the inferior and unreliable forms of calorimeter such as the Lewis Thompson, but to confine attention to one calorimeter in which the fuel is burnt in free oxygen.

Rosenhain Calorimeter.—This apparatus consists of a combustion chamber and a calorimeter vessel in which the water and the combustion chamber are placed. The combustion chamber consists of an ordinary cylindrical lamp-glass chimney which is fitted tightly between two brass plates carrying rubber washers and screws for tightening. Oxygen is passed into the chamber through the inlet pipe at the top and escapes through a ball valve at the bottom and thence upwards through the water in the calorimeter vessel, thus providing efficient stirring. The ball valve prevents the water from entering the combustion chamber, but, when the combustion is complete and it is desired to allow water to enter, the ball is raised.

Procedure.—About 1 gram of the finely powdered coal is pressed into a briquette and placed on the silica tray at the bottom of the combustion chamber. A short length of fine platinum wire is placed across the two terminals in the combustion chamber and the brass plates are screwed together. The platinum wire is made to touch the coal briquette by moving the piece which carries the terminals. 2,500 c.c. of tap water are now measured into the calorimeter vessel, which is then fitted into the wooden case employed to prevent radiation. The oxygen cylinder is then connected to the inlet tube of the combustion chamber and the latter lowered into the water in the calorimeter vessel. The thermometer is introduced into the water, a slow stream of oxygen is turned on, and after a few minutes the initial temperature t_1 and the time are noted. Connection is now made to the accumulators (4 volts) for six seconds. The coal takes fire and burns brilliantly for a few minutes. When the combustion appears to be slowing down the oxygen supply is increased until the combustion is complete. The oxygen is now cut off, the ball valve raised, and the tap at the top of the combustion chamber opened to allow the chamber to fill with water. When full, the chamber is emptied by forcing out the water with a further oxygen supply, the top tap being closed. The maximum reading, t_2, of the thermometer is usually obtained at this stage, and the time also is noted. The apparatus is then allowed to cool for half the time interval between the initial and maximum temperatures, and the observed fall from the maximum temperature is added to the apparent rise in temperature to allow for cooling losses due to radiation. The water equivalent of the Rosenhain calorimeter is obtained by employing a coal whose calorific value is known, as outlined on p. 250.

Example of calorific value of a coal by Rosenhain calorimeter:

1·200 grams of coal taken; 2,500 c.c. of water; water equivalent of calorimeter = 150 grams (water).

	hrs. mins.
Initial temperature at	10·40 = 15·23° C.
Maximum temperature at	10·50 = 18·24° C.
Temperature at	10·55 = 18·22° C.

$$\therefore \text{ Apparent rise } = 18{\cdot}24 - 15{\cdot}23 = 3{\cdot}01° \text{ C.}$$
$$\text{Cooling correction} = 18{\cdot}24 - 18{\cdot}22 = 0{\cdot}02° \text{ C.}$$
$$\therefore \text{ Total corrected rise } = 3{\cdot}03° \text{ C.}$$

$$\therefore \text{ Calorific value of coal} = \frac{(2500 + 150) \times 3{\cdot}03}{1{\cdot}200}$$
$$= 6{,}690 \text{ calories per gram.}$$
$$= 12{,}040 \text{ B.Th.U. per pound.}$$

The principle of the **Bomb Calorimeter** is the same as that of the Rosenhain, but oxygen under a pressure of about 20 atmospheres is employed instead of a stream of oxygen. For details see Brame's *Fuel,* Edward Arnold.

Calculation of Calorific Values.—The calorific value of coal may be *calculated from* the results of the *total analysis*.

The calorific value of carbon is 8,080 calories per gram, and the calorific value of hydrogen is 34,400 calories per gram.

In calculating the calorific value of a coal, however, by this method, allowance must be made for the presence of oxygen in the coal; and it is assumed that only the surplus hydrogen over that required to combine with this oxygen to form water is available for heating purposes.

The available hydrogen is therefore

$$\left(\text{total hydrogen} - \frac{\text{oxygen}}{8}\right).$$

E.g., a coal has the following composition expressed on the dried coal: Carbon 78 per cent., hydrogen 5 per cent., oxygen 12 per cent., nitrogen and sulphur 2 per cent., ash 3 per cent. Calculate its calorific value.

$$\text{Calorific value} = \frac{(8080 \times \text{C}) + 34400\left(\text{H} - \frac{\text{O}}{8}\right)}{100}$$

where C is the percentage carbon,
and H ,, ,, hydrogen,
and O ,, ,, oxygen

$$= \frac{(8080 \times 78) + 34400\left(5 - \frac{12}{8}\right)}{100}$$

$$= \frac{630000 + 120400}{100}$$

= 7,500 calories per gram
or 13,500 B.Th.U. per pound.

The above method of calculation yields only approximate results.

The calorific value of a coal may also be *calculated from the proximate analysis*, though the values so obtained are not always reliable. The calculation and constants were drawn up by Goutal.

Goutal's formula is—calorific value $= 82\text{C} + a\text{V}$ where

C is the percentage fixed carbon;

a is a constant varying with the volatile matter *in the pure coal substance ;*

V is the percentage volatile matter on the whole coal.

The values of the constant a for different values of M (the volatile matter calculated on the dry ash-free coal—*i.e.*, $\text{M} = \frac{\text{V} \times 100}{\text{C} + \text{V}}$) are:

M	5	10	15	20	25	30	35	38	40.
a	145	130	117	109	103	98	94	85	80.

Goutal's formula frequently gives surprisingly accurate results, but as the nature of the volatile products obtained from various coals is liable to variation, the result should always be checked by a calorimeter determination which is really the only reliable method.

Note.—Calorific values are, for scientific comparisons of the organic matter of various coals, frequently expressed on the dry ash-free coal. For commercial purposes the calorific value should be expressed on the dry coal sample, the moisture being a quantity liable to vary with storage, climatic conditions, etc. This is the reason why the percentages of coke, volatile matter, fixed carbon, ash, and total sulphur, etc., are usually expressed on the dry sample.

The Distillation of Coal.—When coal is distilled or heated so that air does not gain access, a certain amount of gases and vapours (which, together, we have called the volatile matter) is liberated and finally a residue of coke is left. The amount and nature of the volatile vapours and gases are governed largely by the pressure and the temperature. If a *low temperature* is employed (up to 450° C.) only a low yield of gas (5,000 cubic feet per ton of coal) is obtained, and it consists principally of methane, ethane, carbon monoxide, carbon dioxide, and olefines (C_nH_{2n}); the volatile vapours on cooling deposit a large quantity (20 gallons per ton of coal) of thin brown tar, lighter than water, and consisting essentially of paraffins (see p. 190). Such tar yields, on redistillation, fractions suitable for motor-spirit, oil-fuel in Diesel engines, etc. The " coke " produced is a " semi-coke " containing 8 to 14 per cent. of volatile matter (at 900° C.) and, if pressed into briquettes before use, yields an ideal smokeless fuel for domestic and other purposes. Distillation of coal carried out below 500° C. is commonly spoken of as the **Low Temperature Carbonisation of Coal.**

If, however, *high temperatures* (about 1,000° C.) are employed, as in *gas-retorts* and *coke-ovens*, the above tar is split up (cracked) in the retorts or ovens as soon as it is produced, and the methane, ethane, and olefines also suffer decomposition. The result is that there is formed only about 10 gallons of thick black tar (heavier than water) per ton of coal. This tar yields, on distillation, principally " aromatic " or " ring " compounds such as benzene, C_6H_6 (see p. 227), and naphthalene $C_{10}H_8$, and the pitch residue (see p. 258) constitutes about 50 per cent. The yield and nature of the gases is also profoundly altered by these decompositions, the yield being more than doubled—12,000 cubic feet per ton—and the composition being that stated on p. 257, showing the presence of about 50 per cent. hydrogen. There is also much free carbon deposited on the crown of the retort as a result of these reactions, and this " retort " carbon is used for making carbon electrodes for electric arcs, Leclanché and dry batteries, etc. The nature of the coke depends largely on the original coal, but prolonged heating at a high temperature tends to give a stronger and metallic-looking coke.

Gas Works.—The processes carried out at gas works and at coke-ovens are essentially the same. " Small " coal is heated in a fire-clay retort which has an exit pipe through which the volatile vapours and gases are drawn off. The heating is continued until no more volatile matter is evolved, and, in the case of coke-ovens, somewhat beyond this stage to produce a better coke. The arrangement of a gas-works plant is indicated in Fig. 94.

Coal is heated in the retorts, *R*, by means of producer gas made in the furnace, by blowing air and steam through red-hot coke. The action of the air may be indicated thus:

$$O_2 + [4N_2] + 2C = 2CO + [4N_2].$$

The action of the steam:

$$H_2O + C = \underbrace{CO + H_2.}_{\text{Water gas}}$$

There is therefore formed a mixture of CO, H_2, and N_2, which is known as producer gas, and this is burned with about an equal volume of air underneath and around the retorts. The temperature reached is about 1,000° C. The volatile matter driven off from the coal consists essentially of water vapour, ammonia, methane, oxides of carbon, hydrogen, and sulphuretted hydrogen, besides much tar, whose composition is discussed on p. 258. These vapours leave the retorts by the ascension pipe, thence to the hydraulic main, and to the condensers where the tar and water vapour are deposited, the water at the same time bringing down much of the ammonia.

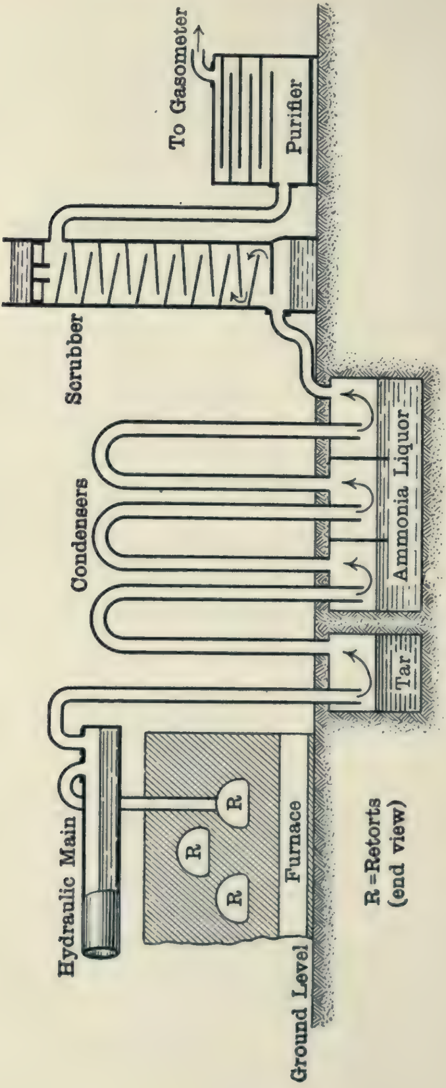

Fig. 94.—Manufacture of Coal Gas.

The gases then pass through an exhauster, not shown (which is a type of fan for drawing the gases from the retorts and forcing them through the various scrubbing and purifying apparatus), after which they are sent through a tar-extractor (not shown), and then through a scrubber, where they come into contact with water and a large area of wetted surfaces which completely extracts the ammonia. It is now necessary to remove the H_2S and the CO_2, as these are undesirable constituents, and this is done by passing the gases through iron cases filled with lime or with iron oxide. The lime extracts both the H_2S and CO_2, whereas the iron oxide extracts only the H_2S (see p. 205). Finally, the purified gases pass through a meter to the gas-holder, whence they are distributed through a governor to the mains. In gas-works practice, 12,000 to 13,000 cubic feet of gas per ton of coal are obtained and about 12 cwt. of gas coke (usually of poor quality) of which about 2 to 4 cwts. are required for making the producer gas.

The Composition of Coal Gas is approximately:

		Gas Leaving the Retorts.	*Purified Gas.*
	H	45	47
	CH_4	32	34
	N	8	8
	CO	6	6
	CO_2	3	2
	H_2S	2	—
	NH_3	1	—
Illuminants such as C_2H_4 and C_6H_6	C_nH_m	3	3
		100	100

The **ammonia,** so far, is contained in aqueous solution in chemical combination as ammonium carbonate, ammonium sulphide, ammonium sulphate, etc. It is obtained free by distilling the aqueous solution with steam, lime being added at the same time. The free ammonia given off is conducted to a lead lined vessel (called a saturator) containing sulphuric acid, with which the ammonia combines, giving ammonium sulphate, a valuable fertiliser:

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

About 25 to 30 pounds of **ammonium sulphate** are usually obtained per ton of coal carbonised. The **tar** obtained is usually about 10 gallons per ton, its specific gravity being 1·1 to 1·2. When distilled it yields a number of valuable products, as may be seen from the following table:

Name of Distillate.	*Temperature.*	*Constituents and Uses.*
Light oil ..	To 170° C.	Benzene, toluene, and xylene. *Uses:* Dyes, explosives, and motor fuel. Toluene → Saccharine.
Middle oil ..	170°–230°	Carbolic acid, cresylic acid, naphthalene. *Uses:* Disinfectants, explosives, dyes.
Heavy oil ..	230°–270°	Naphthalene. *Uses:* Dyes. Creosote oil. *Uses:* Wood preservative, benzol extraction.
Anthracene oil	270°–360°	Anthracene. *Uses:* Dyes, lubrication.
Pitch	Residue	Used for road-making, briquettes.

These fractions have to be purified generally by washing with solutions of (1) sulphuric acid, (2) caustic soda, and (3) water, and then redistilled.

Coal tar yields about the following quantities of commercial products:

	Per Cent.
Benzene, toluene, and xylene	1·5
Carbolic and cresylic acids	0·3
Naphthalene	4·0
Creosote oil	25·0
Anthracene	0·2
Pitch	55·0
Water	14·0
	100·0

Much of the **benzene,** etc., remains in the gas and assists very considerably in improving the illuminating value. With the advent of the incandescent gas-mantle, the illuminating value (candle-power) of the coal gas has become of almost negligible importance; and it is often desirable to obtain large quantities of benzol (*i.e.*, crude benzene) for the manufacture of explosives or for motor spirit, etc. In such cases the benzol is removed from the coal gas by passing the gas through scrubbers of creosote oil, which absorbs the benzol. The creosote oil is subsequently distilled and the lower boiling fractions (viz., benzol) condensed, purified, and redistilled.

At gas works the most successful recent retorts are of the vertical type (Glover West), though the horizontal retorts are more largely in use. In retorts of the vertical type steam is often admitted in small amount towards the end of the coking period. This dilutes the coal gas with water gas ($H_2 + CO$), and gives an increased yield of ammonia (see p. 255).

Coke-Oven Plant.—In the old beehive coking ovens—still largely used—all the valuable by-products are lost; the period of coking is about three days—more than twice as long as with by-product recovery ovens—and the yield of coke is usually below 60 per cent. of the original coal, whereas with recovery ovens the yield is frequently more than 70 per cent. The beehive ovens are about 12 feet in diameter and 8 feet high, and dome-shaped, charged (through a hole in the top) to a height of about 2 feet 6 inches in the oven. The charge is from 6 to 7 tons. The coking is started by the heat from the previous charge, air being admitted through the side door until the bulk of the volatile matter has been driven off, when the side door is sealed and the coke allowed to "bake." The heat is reflected from the dome-shaped roof of the oven on to the coke, and the baking thus proceeds downwards. This results in an excellent coke. When all the volatile matter has been driven off, the door is opened, the coke is quenched (with a hose pipe) inside the oven and then raked out.

The processes at **By-Product Recovery Ovens** are identical in principle with those of a gas works, but the whole operations are on a much larger scale. The charge for each oven is 7 to 10 tons—twenty times the charge for each gas retort—and, in order to obtain a good coke with low ash and low sulphur content, the "small" coal used is generally washed and compressed in a stamping machine before charging into the oven. The ovens are built of fire-brick in batteries of 50 or so, side by side. Each oven is about 6 to 8 feet high, 1 foot 6 inches to 2 feet broad, and about 30 feet long. The ovens are heated by gas derived from the coal in the coking, and there is usually a large surplus which may be used for power or lighting purposes. The ovens are heated by carefully arranged flues underneath and alongside each oven—the flues may be either horizontal or vertical—and in the regenerative ovens the air-supply is preheated, which allows a still greater surplus of gas for power or lighting purposes. The coking period is from twenty-four to thirty-six hours. The coke is pushed out of the oven—there being doors at each end—by a ramming machine, and it is quenched immediately with a spray of water in order to avoid the formation of a brown coating of ash and losses due to combustion.

The yield of coke is about 70 per cent.

The yield of gas is about 10,000 cubic feet per ton of coal.

The yield of tar is about 10 gallons per ton of coal.

The yield of crude benzol is about 2 gallons per ton of coal.

The yield of ammonium sulphate is about 25 to 30 pounds per ton of coal.

In regenerative ovens, of the gas about half is utilised for heating the ovens, which leaves a surplus of some 5,000 cubic feet per ton, suitable for use in gas engines or for heating or lighting purposes.

APPENDIX I

TABLE OF ELEMENTS

Elements.	*Symbol.*	*Atomic Weight.*	*Specific Heat.*
		O = 16	
Aluminium	Al	27·1	0·219
Antimony	Sb	120·2	0·049
Argon	A	39·88	—
Arsenic	As	74·96	0·083
Barium	Ba	137·37	—
Bismuth	Bi	208·0	0·030
Boron	B	11·0	0·254
Bromine	Br	79·92	—
Cadmium	Cd	112·40	0·054
Cæsium	Cs	132·81	0·048
Calcium	Ca	40·07	0·180
Carbon	C	12·00	Variable
Cerium	Ce	140·25	0·044
Chlorine	Cl	35·46	—
Chromium	Cr	52·0	0·104
Cobalt	Co	58·97	0·103
Columbium	Cb	93·5	—
Copper	Cu	63·57	0·093
Dysprosium	Dy	162·5	—
Erbium	Er	167·7	—
Europium	Eu	152·0	—
Fluorine	F	19·0	—
Gadolinium	Gd	157·3	—
Gallium	Ga	69·9	0·079
Germanium	Ge	72·5	0·074
Glucinum	Gl	9·1	—
Gold	Au	197·2	0·032
Helium	He	3·99	—

Elements.	*Symbol.*	*Atomic Weight.*	*Specific Heat.*
		O = 16	
Holmium	Ho	163·5	—
Hydrogen	H	1·008	—
Indium	In	114·8	—
Iodine	I	126·92	0·054
Iridium	Ir	193·1	0·032
Iron	Fe	55·84	0·112
Krypton	Kr	82·92	—
Lanthanum	La	139·0	0·045
Lead	Pb	207·10	0·031
Lithium	Li	6·94	0·940
Lutecium	Lu	174·0	—
Magnesium	Mg	24·32	0·245
Manganese	Mn	54·93	0·122
Mercury	Hg	200·6	0·033
Molybdenum	Mo	96·0	0·066
Neodymium	Nd	144·3	—
Neon	Ne	20·2	—
Nickel	Ni	58·68	0·109
Niton (radium emanation)	Nt	222·4	—
Nitrogen	N	14·01	—
Osmium	Os	190·9	0·031
Oxygen	O	16·00	—
Palladium	Pd	106·7	0·059
Phosphorus	P	31·04	0·202
Platinum	Pt	195·2	0·032
Potassium	K	39·10	0·166
Praseodymium	Pr	140·6	—
Radium	Ra	226·4	—
Rhodium	Rh	102·9	0·058
Rubidium	Rb	85·45	—
Ruthenium	Ru	101·7	0·061
Samarium	Sa	150·4	—
Scandium	Sc	44·1	—
Selenium	Se	79·2	0·084
Silicon	Si	28·3	0·165
Silver	Ag	107·88	0·056
Sodium	Na	23·00	0·293
Strontium	Sr	87·63	—

Elements.	*Symbol.*	*Atomic Weight.*	*Specific Heat.*
		O = 16	
Sulphur	S	32·07	—
Tantalum	Ta	181·5	—
Tellurium	Te	127·5	0·048
Terbium	Tb	159·2	—
Thallium	Tl	204·0	0·032
Thorium	Th	232·4	0·027
Thulium	Tm	168·5	—
Tin	Sn	119·0	0·052
Titanium	Ti	48·1	0·112
Tungsten	W	184·0	0·034
Uranium	U	238·5	—
Vanadium	V	51·0	0·115
Xenon	Xe	130·2	—
Ytterbium (Neoytterbium)	Yb	172·0	—
Yttrium	Yt	89·0	—
Zinc	Zn	65·37	0·093
Zirconium	Zr	90·6	0·066

APPENDIX II

HYGROMETRIC TABLE

Dry-Bulb Reading in Degrees Fahrenheit.	*Difference between the Readings of the Dry-Bulb and Wet-Bulb Thermometers in Degrees Fahrenheit.*													Dry-Bulb Reading in Degrees Fahrenheit.
	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°	11°	12°	
30	100	84	70	58	47	39	32	28	23	18	14	12	10	30
32	100	87	76	65	56	48	41	35	30	27	23	19	16	32
34	100	89	80	71	62	55	49	43	37	33	30	26	23	34
36	100	91	82	74	66	59	53	47	42	38	34	30	27	36
38	100	91	83	76	69	62	56	50	45	41	36	32	29	38
40	100	92	84	76	70	63	58	52	47	43	38	34	31	40
42	100	92	84	77	70	64	59	54	49	44	41	38	32	42
44	100	92	84	78	72	65	60	55	50	46	41	38	34	44
46	100	92	85	78	72	66	61	56	51	47	43	39	35	46
48	100	92	85	79	73	67	62	57	52	48	44	40	36	48
50	100	93	86	79	73	68	62	58	53	49	45	41	38	50
52	100	93	86	80	74	69	63	59	54	50	46	43	39	52
54	100	93	86	80	75	69	64	59	55	51	47	44	40	54
56	100	93	87	81	75	70	65	60	56	52	48	45	41	56
58	100	93	87	82	76	71	66	61	57	53	49	46	43	58
60	100	93	88	82	76	71	66	62	58	54	50	46	43	60
62	100	94	88	82	77	72	67	63	58	55	51	47	44	62
64	100	94	88	82	77	72	68	63	59	55	52	48	45	64
66	100	94	88	83	78	73	68	64	60	56	52	49	46	66
68	100	94	89	83	78	73	69	65	60	56	53	50	46	68
70	100	94	89	83	78	74	69	65	61	57	54	50	47	70
75	100	94	89	84	79	74	70	66	62	59	55	52	49	75
80	100	95	90	85	80	76	72	67	64	60	57	53	50	80
90	100	95	90	85	81	77	73	69	65	62	59	56	53	90
100	100	95	90	86	82	78	74	70	67	64	61	58	55	100

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